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**AEROSPACE STRUCTURAL ADHESIVES**

**NATIONAL MATERIALS ADVISORY BOARD (NAS-NAE)**

**PREPARED FOR  
DEPARTMENT OF DEFENSE**

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study. Conclusions are drawn in each chapter and appropriate recommendations are made.

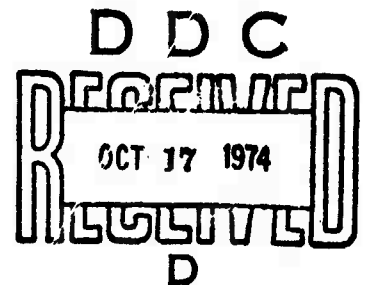
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- Extension of research on the application of fracture mechanics
- Development and perfection of adequate nondestructive test methods
- Development of a better adhesive system
- Expansion of basic studies of physical and mechanical properties
- Continued development and use of better techniques for design and analysis of adhesive-bonded joints.

**AEROSPACE STRUCTURAL ADHESIVES**

**PREPARED BY THE  
AD HOC COMMITTEE ON STRUCTURAL ADHESIVES FOR AEROSPACE USE**

**NATIONAL MATERIALS ADVISORY BOARD  
DIVISION OF ENGINEERING - NATIONAL RESEARCH COUNCIL**



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Dr. Richard F. Blomquist, Chairman  
National Materials Advisory Board  
ad hoc Committee on Aerospace  
Structural Adhesives

## **ABSTRACT**

A study has been made of problems associated with use of aerospace structural adhesives. Consideration is given to the state of the art and future needs in synthesis and formulation of adhesives. The role of interfaces is discussed from a physical chemical point of view. Manufacturing and processing aspects of adhesive use are considered. Data and theory are given for mechanical behavior, permanence, and related areas. Problems of design analysis, specification, and test methods are taken up. Performance, reliability, strategies, and future applications conclude this study. Conclusions are drawn in each chapter and appropriate recommendations are made.

Certain recommendations of relative to broad areas of the subject are considered of approximately equal priority and should receive early serious consideration:

- Development of better means to assemble and communicate information
- Development of a good adhesive manual
- Extension of research on the application of fracture mechanics
- Development and perfection of adequate nondestructive test methods
- Development of a better adhesive system
- Expansion of basic studies of physical and mechanical properties
- Continued development and use of better techniques for design and analysis of adhesive-bonded joints.

(The foregoing is presented in greater detail in Section 2.8)

## PREFACE

The National Materials Advisory Board (NMAB) of the Division of Engineering, National Research Council, National Academy of Sciences/National Academy of Engineering, was asked by the Department of Defense, Office of Research and Engineering to initiate a study of aerospace structural adhesives.

The purpose of this study was to "Initiate a broad survey of adhesives for structural use in aeronautical and space vehicles to identify needs and opportunities (e.g., bonding metal to composites), assess state of the art in adhesives technology (including materials, production costs, application process, data requirements, and methods of test), define problem areas, and describe a comprehensive program of Research and Development for upgrading the technology and accelerating applications where advantage would accrue in performance or economy.

A committee was constituted and began work in May 1972. The study was conducted after presentation of reports by liaison representatives covering needs, views of problem areas, current activities, future plans, and relevant resource material. Tutorial presentations were made by members of the Committee and invited guests.

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## CHAPTER 1

### INTRODUCTION, SCOPE, METHODOLOGY

#### 1.1 Introduction

##### 1.1.1 Definition

A structural adhesive, as distinguished from other adhesives, is one that fastens together elements of a structure. It must, therefore, be capable of transmitting structural stress without loss of structural integrity within design limits. Resistance to the service environment is a corollary property.

##### 1.1.2 Use

It is recognized that when used properly in design structural adhesives frequently afford certain inherent advantages over mechanical fasteners. Among these advantages may be weight saving, electrical and/or thermal insulation, conductivity, fatigue resistance, crack retardance, distribution of imposed stresses, and sealing of voids. In addition to use in aircraft, missiles, and space vehicles (including orbital and reentry vehicles), adhesives are used in surface ships, underwater vessels, land vehicles, and many kinds of building structures. The use of adhesives is growing rapidly but designers lack the definitive approach that gives confidence in routinely incorporating adhesive bonding into design.

#### 1.2 Scope

##### 1.2.1 Focus

The principal focus of the Committee's study is on the use of structural adhesives in aircraft, missiles, and manned and unmanned spacecraft. The stress is on technology, and other considerations are included insofar as they bear on technology.

##### 1.2.2 Exclusions

As stated in the Preface, the Committee believed that its charge was too broad. Accordingly, the Committee deferred consideration, (perhaps by other groups to a future time) of:

- Sealants
- Potting compounds and encapsulants
- Design and processing of advanced composite materials
- Production considerations other than user-related factors (e.g., shelf-life, open time, uniformity, product and process control, joint reliability, etc.)
- Containerization
- Tooling
- Fixtures and assembly jigs
- Optical cements
- Welding
- Soldering
- Brazing
- Diffusion bonding
- Ceramic and inorganic adhesives
- Cost considerations except as generally related to overall mission economic advantage

### 1.3 Viewpoints and Biases

#### 1.3.1 Mission

The requirements for performance and environmental endurance for systems in which adhesive bonding is being considered are given great weight in this study.

#### 1.3.2 Evaluation Criteria

Principal benefits will be sought in performance and/or economic

advantages. In this connection, reliability (the probability of achieving the design-predicted performance) is considered to be a measure of performance. Permanence is another measure of performance when weighed against the mission requirement. In considering use of structural adhesives, non-man rated or remotely piloted vehicles will be considered differently than man-rated vehicles.

### 1.3.3 Approach

A systems engineering approach will be utilized.

## 1.4 Methodology

### 1.4.1 Source Material

Tutorial lectures as well as literature searches have been used to survey the state of the art.

### 1.4.2 Organization

The technical areas to be covered were identified and are designated as Chapters 4 through 10. Chapter 2 extracts principal conclusions and recommendations for the non-specialist or managerial reader. Chapter 3 summarizes government viewpoints.

The reader will find each chapter organized to show scope, state of the art, problem areas, proposed solutions, conclusions, and recommendations (as well as a rough estimate of expected benefits wherever possible). Chapter 2 is a summary of the most important conclusions and recommendations, but full details including supporting information and other recommendations are to be found in the appropriate chapters. It is suggested that the reader consult this information in his specific area of interest.

### 1.4.3 Bibliographic Information

This report is not intended to serve as a textbook. Background material is limited to that deemed necessary to orient the nonspecialist.

Chapters 4 through 10 will serve to direct the reader to current original sources although no claim is made that the literature has been exhaustively surveyed.

## CHAPTER 2

### SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations of the Committee are extensive and, therefore, are grouped in several categories that essentially reflect the subject matter areas treated in detail in the following chapters. Categories include:

- New adhesive systems (Chapter 4)
- Adhesive-adherend interfaces (Chapter 5)
- Manufacturing and processing (Chapter 6)
- Mechanical properties of adhesives (Chapter 4)
- Design, analysis, specifications, and test methods (Chapter 8)
- Performance and reliability (Chapter 9)
- Technology transfer and utilization (Chapter 10)

The individual recommendations within each category are arranged in relative order of priority, as judged by the Committee. The reader is referred to the appropriate chapter for more detailed discussion of each recommendation and its background.

#### 2.1 New Adhesive Systems

##### 2.1.1 Adhesives with Improved Toughness

Conclusion: Structural adhesives for aerospace applications, particularly those recently developed for high-temperature service, generally are too rigid and lack adequate toughness, fatigue resistance, resistance to crack propagation, and moisture stability.

Recommendation: Expand programs on development of new adhesive systems for service at temperatures of 230°C or higher over long periods of time. These adhesives should be suitable for production applications in bonding aerospace hardware and should provide better peel resistance, toughness, and resistance to crack initiation and propagation, improved fatigue resistance, and



greater resistance to organic fluids and moisture in joints, that might be achieved by incorporation of special elastomers or otherwise.

Anticipated Benefits: Such adhesive systems will reduce damage to bonded parts during subsequent machining, cleanup, and trimming and during drilling and attachment of rivets in subsequent assembly operations while still providing inter alia the necessary heat-tolerance and resistance to organic fluids and moisture required by current and future aerospace programs.

#### 2.1.2 Better Adhesives for Honeycomb Core Fabrication

Conclusion: Adhesives presently available for bonding nodes of metal honeycomb core materials by the HOBE process\* involving subsequent mechanical expansion of the bonded metal strips lack adequate peel resistance to withstand this expansion when the stiffer and stronger aluminum alloys are used, particularly for high-temperature service.

Recommendation: Adhesives that provide greater peel resistance and improved heat resistance should be developed for bonding the nodes of high-strength stiff aluminum alloy sheets in the fabrication of expanded metal honeycomb cores by the low-cost and efficient HOBE process. These adhesives must be adaptable to present HOBE-type honeycomb core manufacturing techniques used in making structural sandwich panels for future aerospace applications.

Anticipated benefits: Such adhesives will permit efficient manufacture of high-strength honeycomb cores and will avoid the premature failures resulting from peeling and other stresses. Significant savings in stressed-skin structural panels for aerospace applications should result during both manufacture and service.

#### 2.1.3 Better Structural Adhesives for Cure at Ambient or at Lower Elevated Curing Temperatures than Provided by Present Adhesives

Conclusion : Present structural adhesive systems that are otherwise satisfactory for advanced aerospace applications require curing at such high temperatures that fabrication is difficult or impractical because of the need for

\*See Section 6.4.2.1.8 and Figures 16 and 17 for details on the HOBE process.

special long-cure heating systems while under pressure. In addition, differential thermal contraction creates internal stresses in joints cured at high temperatures when the structure is subsequently cooled to ambient temperature or subjected to actual service at lower than ambient temperature. Further, elevated-temperature curing is not feasible for various necessary repair and modification techniques. Adhesive systems capable of rapid cure at lower temperatures are required.

**Recommendation:** Research and development programs should be initiated to develop improved adhesive systems that cure rapidly at ambient temperature, at moderately elevated temperatures, or via novel mechanisms (e.g., anaerobic curing) without significant sacrifice in strength and permanence of the resultant joints. New polymer systems and related chemical technology should be utilized or developed further to accomplish these objectives.

**Anticipated Benefits:** Development of such structural adhesive systems will permit more efficient, lower-cost fabrication of adhesive-bonded structural assemblies for aerospace, reduce present needs for costly bonding equipment, diminish thermally induced stresses in the resultant joints, and allow more efficient repair and modification, particularly field repairs and modifications in various depots, of bonded assemblies.

#### 2.1.4 Improved Structural Adhesives with Less Critical Application

##### Requirements

**Conclusion:** Many current structural adhesives for aerospace applications require very precise control of fabrication in order to achieve uniform, reliable joint performance. The most widely used presently available adhesives are supplied in film form. There is substantial waste in unused adhesive film on various irregular configurations. Improved adhesive systems that permit more economical and efficient application (as liquids or powders) are needed. (see also Section 2.3.2).

**Recommendation:** Research and development should be undertaken to develop new adhesive systems that (a) require less critical control of all bonding parameters, (b) can be applied to substrates more economically, rapidly, and

effectively than present film systems, and (c) provide the required joint properties.

**Anticipated Benefits:** Development of improved adhesive systems will simplify the production of adhesive-bonded components for aerospace, require less costly and time-consuming control procedures, and make the use of adhesive bonding more feasible and acceptable for a greater number of structural applications than is possible with present adhesive systems.

## **2.2 Adhesive-Adherend Interfaces**

### **2.2.1 Surface Chemistry Aspects of Adherent Surfaces**

**Conclusion:** The nature of the adherend surface influences the initial wetting and subsequent adhesion of the adhesive. In addition, the adherend can influence the physical and chemical properties of the adjacent adhesive at the interface thereby affecting the mechanical properties, the moisture resistance, and other permanence characteristics of the final joint. Techniques for detailed characterization of solid surfaces are now available, are continually being improved, and could be utilized to evaluate, characterize, and improve bonding performance relative to substrate surface properties.

**Recommendation:** Research on surface effects on adhesion, particularly relative to new adherends of interest to aerospace, should be accelerated in order to improve structural bonding.

**Anticipated benefits:** Greater accumulation and use of modern knowledge of adherent surfaces should make the practical production of high-quality structural joints in aerospace hardware most consistent and more reliably and should result in joints meeting future critical performance requirements for bonded assemblies.

### **2.2.2 Surface Treatments of Adherends for Bonding**

**Conclusion:** According to the nature of the material, various metal alloys and plastic composite materials require individual methods for proper preparation of the adherend surface for adhesive bonding. Different adhesive manufacturers now often prescribe different techniques and processes for preparing the same adherend for bonding with their particular adhesive systems. Many of the prescribed techniques are based on empirical knowledge rather than on sound

scientific knowledge of the surface. It is recognized that such surface preparation techniques can influence not only the initial adhesion, but also the subsequent durability of the joint and performance in service at elevated temperatures and under moisture and salt-spray conditions. A good beginning toward an accepted practice for adherend surface preparation is in ASTM D2093, D2094, D2651.

Recommendation: Standard surface treatment practices that are usable for all adherends of major importance in aerospace structural bonding should be developed and their adequacy established.

Anticipated Benefits: Development of standard practices for surface treatment of a wide variety of adherends of importance to aerospace structures will simplify production techniques and control of bonding applications, produce more uniformly reliable joints of high quality, and reduce production costs.

## **2.3 Manufacturing and Processing**

### **2.3.1 Weldbonding Technique**

Conclusion: Weldbonding is a system of spotwelding two adherends together at several points after adhesive application and before curing to provide some bonding pressure internally, thus eliminating the need for complex pressure-application techniques during curing. This technique offers advantages in simplified production with certain types of structural adhesives. It promotes static strength through the weld and fatigue strength through the adhesive bond.

Recommendation: The weldbonding technique should be further developed to be applicable to a wider range of structural adhesives for bonding a variety of metals for aerospace applications.

Anticipated Benefits: This technique can provide a simpler fabrication technique for structural metal bonding by providing the necessary pressure to hold the adherends together adequately during curing at ambient or elevated temperatures, thus eliminating the need for special presses, clamps, and bags to provide holding pressure until the adhesive develops adequate cure. This can save production time, avoid need for costly equipment, reduce costs of bonding, and markedly improve the fatigue life of structures over those joined only by spot-welding or adhesive bonding alone.

### 2.3.2 Improved Adhesive Application Techniques

Conclusion: Present methods for applying liquid and powder adhesives to substrates are limited to spraying or roller coating, both of which are slow and require careful control. Liquid adhesives present problems involving entrapped solvents and inclusion of condensed atmospheric moisture; several coats generally are required to provide the necessary weight of adhesive for adequate bonding, and they are typically applied in batch-type operations.

Recommendation: Development of advanced techniques, such as electrostatic deposition, for applying adhesives to substrates should be continued to provide more rapid, uniform, and economic procedures and to provide higher quality bonds. Emphasis should be given to development of new liquid and powder adhesive systems in bulk form to replace the expensive film and tape adhesives now used (see also Section 2.1.4).

Anticipated Benefits: Development of improved adhesives systems and application techniques will provide more rapid production of bonded assemblies, will reduce adhesive waste (thus reducing cost) and when properly developed, can improve the uniformity and reliability of bonded joints in a variety of complex assemblies for aerospace applications.

### 2.3.3 Improved Techniques for Machining Advanced Composite Bonded Assemblies

Conclusion: Present methods of machining advanced composite bonded assemblies in final manufacturing are time consuming, costly, and often tend to damage the joints.

Recommendation: Better methods and techniques should be developed for machining bonded composite assemblies after the adhesive has been cured in order to reduce machining time and costs, eliminate requirements for costly special tools and special skills, and minimize or eliminate mechanical damage to the bonded composite assemblies.

Anticipated Benefits: Development and use of such improved machining techniques will reduce costs of making the complete composite bonded assemblies

and provide quality assemblies more predictably by reducing mechanical damage from machining after bonding.

#### **2.3.4 Preforming of Metal Adherends for Bonding**

**Conclusion:** Many metal parts for aerospace assemblies involve curved and other special shapes and contours rather than flat sheets. The manner in which these adherends are shaped or formed can affect the subsequent quality and uniformity of the bonds, both by influencing the fit of the two adjacent adherends in the joint and by modifying the nature of the surface offered for bonding.

**Recommendation:** Investigations should be undertaken to develop reliable methods of analyzing nonplanar adhesively bonded joints, both as a function of geometry and as a function of method of forming, to determine the resultant strength and durability of the adhesive bonds and to find solutions for any adverse problems noted.

**Anticipated Benefits:** Knowledge developed from these investigations will overcome the problems often encountered in preforming metal adherends (such as modification of adherend surfaces, inadequate fit of joints to permit proper bonding, bonds of erratic and/or inadequate or excessive thickness) and therefore, will reduce the fraction of rejected assemblies as well as the amount and cost of adhesives used.

#### **2.3.5 Contouring Surfaces of Honeycomb Cores for Improved Bonding**

**Conclusion:** Many bonded aerospace assemblies, such as control surfaces of wings and rotors, are of unusual configurations with non-planar skin surfaces in sandwich-type panels. Such applications require that the honeycomb cores be contoured to various shapes and contours before bonding. Present methods for such shaping are generally inadequate, costly, and erratic and may affect subsequent adhesive bonding quality and uniformity.

**Recommendation:** Better methods should be developed as alternatives to the present honeycomb surface machining techniques, and their effects on the subsequent quality of adhesive-bonded sandwich panels should be established.

**Anticipated Benefits:** Development of improved shaping and contouring

techniques for honeycomb cores prior to bonding and the establishment of their adequacy for the more critical aerospace assembly requirements will reduce the need for present slow and costly surface machining techniques, improve the quality and uniformity of the bonded assemblies, and permit the production of unusual shaped sandwich panels not presently possible with adhesive-bonding techniques.

#### 2.3.6 Processing Specifications

Conclusion: The quality of any adhesive joint depends both upon the quality of the adhesive and on the way in which it is used in bonding. Since continuous nondestructive testing of all bonded assemblies is not yet feasible, the best way to provide uniformly adequate bonds for aerospace applications is by close process control. This requires carefully prepared process specifications for each process step and close following by an adequate control program. At present, processing specifications are prepared separately for each different adhesive, and generally somewhat different specifications are developed and used for the same adhesive by different manufacturers of bonded products.

Recommendation: It is recommended that an impartial<sup>+</sup> review be made of the various adhesive processing specifications for different structural adhesives now used in the aerospace industry and that an effort be made to produce a standard recommended practice for application and for use of structural adhesives for the entire aerospace industry.

Anticipated Benefits: The development and use of a standard recommended practice for the application and use of structural adhesives, even a separate specification for each type of adhesive, on an industry-wide basis would improve process control in production of bonded aerospace assemblies, enhance uniformly adequate quality, and reduce the duplication of effort in the development of additional individual specifications. In addition, the cooperative efforts by different firms in the aerospace industry in developing such a standard could result in better industry performance by pooling all of the strong points of the individual contributors.

## 2.4 Mechanical Properties of Polymers and Adhesives

It is worth noting that in most early research on adhesive bonding, great emphasis was given to the nature of adhesion to various substrates and much concern was expressed over achieving good adhesion in bonding. Extensive practical experience suggests that adhesion is not often a serious problem in bonding applications with typical metal and other adherends but that the adhesive film typically fails cohesively in the joint under various loads and test conditions. It is only recently that the adhesive film has been recognized as a material in its own right and that the physical, chemical, and mechanical properties of such a film are critical in determining the performance of joints. Hence, this subject is of great current importance in modern structural adhesive bonding technology.

### 2.4.1 Basic Material Properties of Adhesives

Conclusion: In order to design structural bonded joints effectively the designer needs fundamental data on basic static and dynamic mechanical properties of adhesives in joints, considering the adhesive film in such joints as a separate engineering material like the adjacent adherends.

Recommendation: Previous and ongoing research programs should be amplified to provide basic material properties information for selected structural adhesives to include reliable data for designers on Young's modulus, yield stress, tensile strength, extensibility, creep and other time-dependent properties, thermal expansion and related thermal properties, and chemical reactivity as a function of time, temperature, and service conditions expected in the bonded joints.

Anticipated Benefits: A needed comprehensive experimental approach will provide more useful data for engineers, and a basis for designing improved joints scientifically rather than, as at present, empirically.

### 2.4.2 Correlation of Mechanical Performance of Bulk Polymers and Adhesive Films with Basic Property Data

Conclusion: A great deal of basic information is available on the mechanical and physical properties of a wide variety of bulk polymers and formu-



lation of these polymers as plastic materials. Little information is available on the correlation of such bulk properties and the corresponding properties of adhesive systems of the same compositions when present as thin films in an actual bonded joint. It is recognized that the presence of the adjacent adherends, and the conditions under which the bond is formed in these joints, can alter the properties of the polymer system as compared to those cured as isolated films or bulk polymers.

Recommendation: It is recommended that a comprehensive, long-range, unified research program be initiated to correlate the performance of polymeric adhesive compositions in bulk and in a bonded joint. This should involve stress analysis; fracture mechanics and consideration of the mechanisms of setting, curing, and hardening of the adhesive; effects of morphology and composition of the adhesive surface-induced phase separations; and environmental interactions.

Anticipated Benefits: If one knew more about the possible correlation of the mechanical and related physical properties of an adhesive formulation in bulk and in the bonded joint, one could more adequately predict the mechanical behavior of the joint from bulk properties, which are often more simple to determine, and from already existing data. If mechanical properties of films in actual joints could be reliably predicted from bulk properties, the development of additional data on the mechanical properties of other structural adhesives from such bulk properties could be simplified and a large element of uncertainty could be removed from design use of adhesive-bonded joints.

#### 2.4.3 Microfracture and Fracture Mechanics

Conclusion: Studies of induced microfractures and faults and their rates of propagation in metals and plastics have proved invaluable in understanding the fundamental nature of mechanical failure in such materials, in predicting these failures, and in reducing and eliminating them. This technique has only recently begun to be applied to adhesive bonding problems. Design engineers need to understand the importance of microfractures in adhesive joints, to have the necessary basic data and knowledge required to design better adhesive-bonded joints for critical aerospace applications, and to predict more reliably possible failures in service.

**Recommendation:** It is recommended that research efforts be expanded to study fracture in adhesive joints, emphasizing the application of modern fracture mechanics techniques for predicting joint performance. Special attention should be given to correlating theoretical and experimental studies of the loci of crack initiation in the adhesive and at the interface and the rate of propagation of such microcracks as a function of adhesive composition, bonding conditions, joint configuration, loading conditions, and environmental exposure, with special emphasis on fatigue behavior of the joints. Special attention also should be given to potential benefits of fillers and rubbery inclusions in strengthening such polymeric structural adhesives.

**Anticipated Benefits:** Knowledge gained by these studies will permit: (a) a more efficient approach to polymer synthesis and adhesive formulation for improved adhesives for structural use in joints of various designs and under various loading conditions, including peel, impact, and fatigue conditions, that provide greater toughness and resistance to crack initiation and propagation, and (b) the design of more efficient joints for critical applications. Greater knowledge and understanding of the role of fracture mechanics and the factors that influence the initiation and propagation of microcracks in adhesives in joints will provide a very valuable tool to correct these adverse factors and influences that cause microfailures in actual joints under various loads and environments and in different joint configurations. These findings should be translated into suitable design charts and graphs that can be used effectively by engineers in better designs of adhesive-bonded joints.

#### **2.4.4 Standard Design Techniques Based on Fracture Mechanics**

**Conclusion:** Design engineers in the aerospace industry need to know more about the application of the principles of fracture mechanics in design of improved joints and bonded assemblies, as well as more about microfractures, to supplement conventional engineering design procedures for the design of better joints.

**Recommendation:** Standard experimental techniques for evaluating fracture mechanics characteristic of adhesives in joints of various configurations need to be developed and accepted widely. These techniques then must be taught to design engineers and used to develop an adequate library of design data for use by aerospace design engineers in producing designs that can reduce failures in bonded joints.

**Anticipated Benefits:** Development of the necessary basic data and wide understanding and acceptance of the principles of micromechanics and fracture mechanics in design of adhesive-bonded assemblies and prediction of failures can provide aerospace design engineers with a very valuable tool for production of better bonded assemblies for critical applications.

#### 2.4.5 Stress Analysis of Joints

**Conclusion:** Information is needed to provide for a further understanding of the role of modifications in conventional structural adhesive formulations in influencing the stresses in adhesive joints.

**Recommendation:** Research on theoretical analysis of stresses in various joint configurations, including the effects of layered adhesives, presence of flaws, voids and unbonded areas, rough interfaces, deformable adherends, and elastic-plastic behavior of the adhesive and/or the adherend should be strongly supported.

**Anticipated Benefits:** A clearer understanding of the roles of the mechanical properties of the adhesive relative to those of the adherend, determinate and indeterminate flaws and imperfections in the adhesive film, and the interface with various joint configurations can result in a more scientific approach toward developing better adhesive formulations and bonding processes that will provide uniformly adequate and reliable structural bonds for critical aerospace applications.

#### 2.4.6 Effects of Environmental Factors on Joints

**Conclusion:** Water and water vapor are known to be deleterious to certain types of adhesive joints with metals and other adherends. These effects seem to be quite specific for the adhesive-adherend combinations.

**Recommendation:** Research should be expanded to elucidate the mechanisms by which environmental agents such as water and water vapor affect the properties of structural adhesives and bonded joints. Emphasis should be given to both physical and chemical factors and to specific interfacial reactions. Mechanical studies in joints should be coupled with chemical studies of changes in the adhesive films.

**Anticipated Benefits:** Studies should provide valuable insight into the reasons why adhesive bonds fail under the influence of water and water vapor, as influenced by the adhesive-adherend combination, and thus provide means to improve performance of structural joints in aerospace assemblies subjected to such environmental influences.

## 2.5 Design, Analysis, Testing, and Specifications

### 2.5.1 Design Specification

**Conclusion:** Design specifications for adhesive-bonded joints and components are now developed separately as needed for each specific application by each aerospace contractor. This results in much duplication of effort and a general lack of continuity from one development to another.

**Recommendation:** After canvassing the major users and investigators of adhesive-bonded structures for available information and recommendations, an industry-wide design specification for adhesive-bonded aerospace structures should be developed. This effort probably will identify gaps in available knowledge and will serve as a useful preliminary design guide; in addition, it can serve to stimulate the development and accumulation of the additional information needed. (See also Section 2.7.2, Adhesive Handbook.)

**Anticipated Benefits:** This design specification or guide will serve as a useful means for unified design approach for adhesive-bonded structures for aerospace, as a useful training tool for new design engineers, to bring together the extensive scattered knowledge of design procedures for complex bonded assemblies, and to identify missing information that must be developed to meet the future needs of aerospace design engineers.

### 2.5.2 Stress Concentrations in Joints

**Conclusion:** Stresses exerted on adhesive-bonded joints, either internally from

thermally induced dimensional changes or from external loading, critically affect ultimate joint performance. Distribution of these stresses is dependent on joint dimension and geometry. Much more must be learned about these stress distributions and the factors that can be used to minimize and control them in various joint configurations. Computer-aided design analysis is an important tool for employing the knowledge of stress distribution.

Recommendation: The present theoretical closed-form solutions to differential equations, which predict stress distributions in various configurations of bonded joints (i. e., single overlap, double overlap, stepped overlap, scarf overlap and butt joints) should be refined and expanded systematically and new solutions obtained. Present solutions should be expanded to include cases in which the adherends are either the same or different in thickness and composition, in which the adherends exhibit either elastic or plastic behavior, and in which temperature and thermal residual stress considerations can be superimposed on static loads. The applicability of such computer-assisted techniques to evaluate various more complex adherend shapes and boundary conditions should be demonstrated. This information should be incorporated in the Adhesives Handbook (see Section 2.7.2).

Anticipated Benefits: Establishing the utility and validity of such complex modern computer-assisted analyses of stress distributions in bonded joints of various materials and configurations, when under various external and induced loading conditions, will be an extremely valuable design tool for present and future aerospace engineers.

### 2.5.3 Mechanics and Modes of Failure in Bonds

Conclusion: Designers in the aerospace industry need additional data on factors that influence actual failures in bonded joints.

Recommendation: Theoretical analyses, verified by experiment, of the mechanics and modes of adhesive failure in joints when subjected to ultimate static loads, impact, cyclic, creep loads, and loads at various temperatures should be initiated. These findings should be translated into design charts and graphs that can be used effectively by engineers in producing better designs of adhesive bonded joints.

**Anticipated Benefits:** Results of the proposed investigations will provide design engineers with valuable new tools for designing joints for aerospace applications that minimize failures under anticipated load and service conditions.

#### **2.5.4 Time-Dependent Effects in Design**

**Conclusion:** While much data and many techniques exist for design of bonded joints under static loading, new data are required to consider loadings that are time dependent.

**Recommendation:** Studies should be initiated to extend and expand current theoretical analyses of statically loaded bonded joints to include time-dependent effects, such as crack propagation, creep, impact, and fatigue.

**Anticipated Benefits:** Development of this information will permit the design engineer to predict more accurately the performance of the adhesive-bonded joints under dynamic conditions of loading and, hence, improve the reliability of the bonded assemblies in actual service.

#### **2.5.5. Fracture Mechanics as a Design Tool**

**Conclusion:** The relatively new field of fracture mechanics offers the designer an additional valuable tool in designing bonded joints for critical aerospace applications; it currently is not being used extensively or effectively in joint design.

**Recommendation:** Research should be expanded in the rapidly growing science of fracture mechanics. Understanding should be disseminated of advances in improving joint performance. Special emphasis should be given to minimizing initiation and propagation of cracks in adhesive films and adjacent adherends during both bond production and actual service. Instructional teams should be established to teach designers and engineers in the aerospace industry of the importance and use of fracture energy criteria in joint design.

**Anticipated benefits:** This is a critical need. While much is known about the use of fracture mechanics principles in other materials, little is known about their application to adhesives in joints. The information is widely scattered and many design engineers are unfamiliar with this new field. Intensive training based on necessary background data can provide the design engineer with a valuable tool to augment

traditional design techniques and improve the reliability of bonded assemblies for aerospace.

#### **2.5.6 Selection of Composites to Improve Bond Performance**

**Conclusion:** Many of the newer composites, such as fiber-reinforced plastic materials intended for special high performance under very high or very low temperature conditions, often fail cohesively when bonded to another adherend.

**Recommendation:** Select from the most promising composites\* those whose tensile, interlaminar shear, and related strength properties equal or exceed the corresponding properties of the structural adhesives used to bond such assemblies.

**Anticipated Benefits:** If the cohesive strength properties of composites to be bonded in a complex assembly can be improved without adversely affecting the primary properties for the final application, it will be possible to produce bonded joints in these assemblies that will have much higher load tolerance, will take advantage of the higher strength properties of the adhesive, and will reduce premature failure in the composite material in service.

#### **2.5.7 Reducing Failures at Interfaces in Bonded Composites**

**Conclusion:** Many advanced composites to be bonded have thermal expansion characteristics widely different from metals used in the same joints (creating a problem closely related to that described in Section 2.5.6). Techniques are needed to reduce stress concentrations resulting in premature cohesive failure in special composites, near the adhesive bond line, but actually in the composite adherend when the joint is loaded or subjected to thermal stresses.

**Recommendation:** Investigation should be initiated of the "graded seal" concept, whereby one or more thin layers of suitable modifying material are sandwiched into the bond lines of bonded composite assemblies in order to reduce undesirable effects of large differences in coefficient of thermal expansion.

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\* Resistant to cleavage and shear stresses in the immediate vicinity of the bond line.

**Anticipated Benefits:** Practical and reliable techniques to modify the bond-line stress concentrations between such dissimilar adherends as boron composites and steel or aluminum by modification of the bond line itself could provide the designer and fabricator with a valuable tool to produce stronger and more predictable bonded assemblies needed for advanced aerospace applications.

#### **2.5.8 Modification of Joint Design for Different Adherends**

**Conclusion:** When joints involve the bonding of adherends that have considerably different stiffness characteristics, excessive stresses build up in the joint. These induce premature failure in the joint, typically in the adhesive layer.

**Recommendation:** Methods that promise to minimize stress concentrations by tailoring the bond lines between adherends of widely different stiffness should be investigated. Possible approaches include scarfing stiffer adherends, locally building up the softer adherend, incorporating two or more layers of adhesives with different stiffness in the joint and using more widely the "graded seal" concept.

**Anticipated Benefits:** Practical solutions to improving design and fabrication techniques for assemblies of two adherends of widely different stiffness by minimizing internal stress concentrations, either from thermally induced or mechanically loaded sources, will improve joint strength and, hence, the overall quality and reliability of the bonded assembly.

#### **2.5.9 Improved Shear Tests**

**Conclusion:** At present most strength data on structural adhesives have been developed with the thin-adherend lap-shear test procedure\* that, while entirely satisfactory for comparative adhesive evaluation and for quality control in production and acceptance of adhesives, is recognized as inadequate in providing true shear data. Other shear tests for adhesives in joints, such as the torsional ring or "napkin ring" test are complicated and costly. Better shear data on

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\* ASTM D-1002.



adhesives is needed by design engineers.

Recommendation: New studies of the thick-adherend lap-shear specimen, with various geometric dimensions, different adherends, and other test variables, should be initiated and resultant information should be optimized to develop an acceptable standard test specimen and method that provides design engineers with shear data on adhesives more useful than the conventional lap-shear data currently available.

Anticipated Benefits: Development of a relatively simple, reliable test method to provide adequate shear data on structural adhesives can equip aerospace designers with the necessary data for design of better bonded assemblies than are currently possible; it would take much of the empiricism out of design of sophisticated assemblies, giving designers greater confidence in adhesive bonding.

#### 2.5.10 Determination of Strain in Joints Under Loads

Conclusion: To determine the actual stiffness of adhesives, as well as to study their performance in actual joints under loads, better methods are needed to measure strains in the actual bond lines under a variety of loading conditions. It is not sufficient to use conventional extensometers across the entire bonded assembly.

Recommendation: Instrumentation and techniques that more effectively determine strain under load in tests of adhesive-bonded specimens should be developed to provide reliable stress-strain data for design purposes. Such instruments (extensometers) must be usable at temperatures from -55 to 82°C and must be rugged enough to withstand impact and extreme elongation when the specimen fails.

Anticipated Benefits: Development of suitable instrumentation for measuring strains in the adhesive under different loading up to actual failure will permit reliable measurement of stress-strain behavior of structural adhesives under various environmental conditions. This will permit computation of reliable moduli values for design purposes as well as more reliable prediction of the performance of adhesive joints under a variety of stresses.

## **2.6 Performance and Reliability**

### **2.6.1 Nondestructive Test Techniques**

**Conclusion:** The current principal means for assuring quality of bonded assemblies in actual production is a costly quality-control program over all phases of the bonding process. It is impractical to test the bonded parts to destruction before acceptance, and proof loading of these parts is only of limited value. Non-destructive testing of bonded assemblies on a routine, full-scale basis is greatly needed. Present nondestructive test procedures are limited essentially to distinguishing between bonds of different quality.

**Recommendation:** Effective, low-cost nondestructive inspection and testing systems for bonded panels and assemblies that can assess bond strength and not merely detect unbonded areas should be developed. Such methods should be suitable for rapid and precise scanning of entire bonded panels and assemblies on a 100-percent inspection basis.

**Anticipated Benefits:** When established and validated, an effective, nondestructive inspection system would ensure that any accepted bonded assembly met the design strength criteria, thus greatly improving the confidence of design engineers in adhesive bonding as well as insuring the performance of such assemblies in service.

### **2.6.2 Predicting Long-Term Service Life**

**Conclusion:** Predicting the permanence (long-term serviceability) of bonded joints is one of the most difficult tasks in adhesive technology. The continued introduction of new polymer systems, new formulations of these polymers with a wide variety of other components, the variations in the entire bonding process, and the use of structural adhesives in numerous joint configurations and with different adherends, all complicate the problem of predicting long-term serviceability. One cannot wait for long periods of demonstrated service before deciding to use a new adhesive system. Short-term tests that reliably correlate with actual service are badly needed. Fortunately new statistically oriented techniques, based on physical chemical developments, offer some real promise to solve this problem.

**Recommendation:** The general statistical and physical chemical theories

of cumulative damage should be reviewed and evaluated thoroughly for applicability in predicting the long-term service life of adhesives and bonded joints and structures. Better methods for accelerated service tests of adhesives and bonded joints based on these principles should be investigated. Particular attention should be given the potential of the Weibull cumulative distribution function as a major improvement over the normal Gaussian function for statistical determinations of anticipated service life of bonded joints.

Anticipated Benefits: The development of reliable techniques for estimating the long-term service life of structural adhesives and bonded assemblies will permit design engineers to confidently produce a wider range of sophisticated designs and provide assurance that these bonded products will withstand the rigors of anticipated service. Predictive techniques also will be invaluable to adhesive developers as a means of rapidly establishing the permanence of new structural adhesives during the development stages and can serve as appropriate tests for inclusion in adhesive procurement specifications.

## 2.7 Technology Transfer and Utilization

### 2.7.1 Wider Use of Present Adhesive Technology

Conclusion: The literature on adhesive technology and application is currently widely scattered. Much of it is unpublished and/or retained by individuals and organizations who have developed the information for their own specific needs. As a result, a great deal of the existing knowledge is not being widely used. There is much duplication of effort in collecting the same information independently. This seriously retards the wide use of structural adhesives in all applications and particularly in the aerospace industry. Further, design engineers often are unfamiliar with this literature on adhesives and, therefore, do not consider the use of structural adhesives where their use might upgrade the design of aerospace hardware.

Recommendation: One or more techniques should be developed and initiated for getting current knowledge on structural adhesives and their aerospace applications into wider, more immediate and effective use. This can include an

adhesive design and fabrication manual (see Section 2.7.2), training courses, symposia, field instruction teams, improved publications, and information retrieval and dissemination systems (e.g., an Information Analysis Center).

**Anticipated Benefits:** This is a basic recommendation including several elements of more detailed recommendations that follow. All phases of this approach will help overcome the difficulty in getting present knowledge of adhesives and their applications into more prompt and efficient use in the aerospace industry. It also should be recognized that such information can be of direct benefit to other U.S. industries and to the nation's economy.

#### 2.7.2 Adhesive Handbook

**Conclusion:** One of the best techniques for broadening the use of structural adhesives and bonding techniques would be to assemble all the most pertinent and applicable information into a single document for widespread use in an efficient manner.

**Recommendation:** An effective handbook of adhesive bonding and design, including available information on basic mechanical and performance properties and all design parameters of typical structural adhesives should be developed. It also should include available information on joint design concepts, techniques for structural analysis of joints and assemblies, tooling concepts for production, processing information, and estimated costs for manufacturing typical bonded assemblies. This handbook must be made easily available for wide distribution and use and must be kept up to date through appropriate revisions (e.g. Mil Hdbk. 15-A).

**Anticipated Benefits:** This type of handbook would be of immense value not only to the aerospace industry but to the civilian industries and to engineers and scientists generally. It would provide basic data and knowledge on adhesive bonding in much the same manner that is now provided for concrete, steel, aluminum, and other construction materials. Thus, designers and engineers would have the necessary information available in a single reliable source, and this would certainly advance the intelligent and effective use of structural adhesive bonding.

### 2.7.3 Training of Future Personnel

Conclusion: At present there are no effective formal training programs for individuals in adhesive science and technology at the college, university, or technical levels. Workers entering the structural adhesives field are trained either in the basic sciences or engineering, with little or no special introduction to the field of adhesives. There also is little or no attention given to training of technicians in this field.

Recommendation: Instructional material, suitable for use in engineering and related university-level instruction, should be developed and made widely available to advance and strengthen the future training of engineers and materials scientists in structural adhesive bonding. Appropriate courses should be organized for technician training. Strong efforts need to be made to insure that appropriate courses of study, based on such instructional materials, are presented effectively at the university and other levels and that these courses are kept up to date with the advances in science and technology in this field.

Anticipated Benefits: Training and instructional material can provide a pool of adequately trained engineers, scientists, and technologists for the future aerospace industry, thus assuring that future generations can, and will, use adhesive bonding to its full potential for the nation's benefit. Such training also will provide a much improved base for future researchers in adhesives science and technology.

### 2.7.4 Short-Term Instruction Programs

Conclusion: There is a great need for immediately updating the knowledge and training of individuals now involved in structural adhesive applications in the aerospace industry.

Recommendation: A competent instructional team comprised of two or three experts in various phases of adhesive-bonding techniques and production of bonded aerospace assemblies should be assembled and sent out to present comprehensive short courses in various manufacturing centers to update designers, process engineers, and materials specialists in current adhesive

technology and applications on a continuing basis. Later the activities of a team or teams might be expanded to provide limited expert consulting services on specific bonding problems and applications.

**Anticipated Benefits:** A program of this type would provide immediately a needed effective means to bring the most pertinent knowledge on adhesive technology, directly related to aerospace applications and problems, to those most in need of this knowledge. Thus, it would serve as a stop-gap program until the more formal training courses previously proposed are well established. Short course training programs could well be continued later to update knowledge effectively and rapidly. These courses also would provide a valuable forum for interchange on current problems for which effective solutions are not readily available. Such problems then should be properly communicated to researchers active in the adhesives field.

#### **2.7.5 Central Information Center on Structural Adhesives**

**Conclusion:** It would be highly desirable to have one central depository for information and data on all aspects of adhesive technology and design so that users of this information could readily locate and retrieve it.

**Recommendation:** One competent organization should be selected and designated to serve as a centralized information center for all published and documented information on structural adhesives and their applications. Primary access to these services should be available on a minimum or no-cost basis only to domestic industries and related investigators. It is recommended that PLASTEC at Picatinny Arsenal be selected for this function.

**Anticipated Benefits:** A central organization would provide a well-recognized, readily accessible source of up-to-date information and data on all phases of adhesive technology and application. This would save a great deal of time and effort in searching and retrieving the extensive literature on the subject and would ensure that new literature was incorporated in the system on a continuing basis.

#### **2.7.6 Symposia, Technical Meetings, and Societies**

**Conclusion:** Although individual papers are given and discussions on adhesive subjects are presented at meetings of various technical societies and organizations, they tend to become lost among a large group of other topics and therefore are not adequately publicized. In addition, the present dispersal of these presentations makes it impractical for the serious structural adhesives researcher or practitioner to attend these meetings just to hear one or two papers. More importantly, these meetings do not bring together a large enough group of individuals with broad experience in adhesive technology to provide an adequate forum for informal discussions of related matters and experience (that is often more valuable than actual papers). Better forums for exchange of information between people active in the adhesives field are needed.

**Recommendation:** Appropriate technical societies and journals should be encouraged to organize and present information, including a series of technical symposia, on the design, manufacture, and production/cost interfaces in bonding of structural assemblies for aerospace, updating and revising this information continuously as new knowledge and technology are assembled.

**Anticipated Benefits:** Organization of symposia and other technical meetings devoted specifically to adhesive technology would serve as an important means to disseminate new knowledge and would provide a very useful forum for active individuals in the adhesives field to exchange data and ideas, thus serving to advance the state of knowledge and experience in adhesive bonding most effectively.

## 2.8 Order of Priority for Recommendations

The Committee found that it was very difficult to attempt to provide an overall priority rating system for various recommendations indicated in this report. Accordingly, no priority ratings are given. As previously indicated, the recommendations under each chapter are listed in approximate order of urgency, recognizing that it may be impractical to develop and finance research and development programs for investigating each problem in the indicated order. Some problems are amenable to simple or short-term solutions; others will

require a much more extensive and costly effort. Rather than attempt to propose a definite order of priority, the Committee wishes to propose that the following broad areas, each covered by one or several separate recommendations, should have almost equal priority and receive early serious consideration to find resources to implement them. These areas are as follows:

- Development of better means to assemble and communicate information on structural adhesives on a continuing basis in order that such information is put into practice as early as possible.
- Development of a good adhesive manual, or series of manuals, to include all pertinent information on design, fabrication, and application of structural adhesives, with special emphasis on aerospace and process control.
- Extension of research on the application of fracture mechanics to the design and production of bonded joints and acceleration of efforts to inform design engineers of the potentials and principles of this technique and to provide them with the necessary data to allow this to be put into practice without delay. Especially needed is information on stress rupture and fatigue.
- Development and perfection of adequate, reliable short-term test procedures for predicting service life of bonded joints.
- Development of adequate nondestructive test methods to identify acceptable bonded joints on a continuous basis. These methods would be immediately put into use, (e.g., in the aerospace industry).
- Development of better adhesive systems offering (a) faster and lower temperature curing, and (b) improved toughness and related dynamic properties for service at high temperatures and over a wide range of service temperatures. Of particular note is the weldbond technology.
- Expansion of basic studies of the physical and mechanical properties of structural adhesives as bulk materials in joints, with special



emphasis on their role in controlling micro-fractures, crack initiation and propagation and on improving the energy-absorbing characteristics of the actual adhesive film in the joint, particularly under dynamic loading and under time-dependent conditions where many current adhesive systems have serious limitations.

- Continued development and use of better techniques for design and analysis of adhesive-bonded joints, using modern computer-assisted techniques not formerly practical, in order to provide design engineers with techniques and data to design highly stressed bonded assemblies for aerospace applications with greater confidence. This includes experimentation to develop more adequate data on design parameters, including better shear data, and on performance under dynamic loading of various types, including fracture mechanics techniques.

## CHAPTER 3

### CURRENT AND FUTURE SERVICE APPLICATIONS

#### 3.1 Introduction

##### 3.1.1 Purpose, Methodology, and Perspective

The purposes of this chapter are to review previous, current, and future applications of structural adhesive bonding for aerospace systems and to assess the needs and potential for further exploitation of this technology in aerospace systems. This is done by (a) citing representative successful applications of adhesive bonding, (b) pointing out problems that have restricted adhesive bonding, and (c) describing in detail the needs and advances required in adhesive bonding technology for aerospace applications that can be envisioned for the government services in the next decade. The chapter perspective is that structural adhesive bonding is a viable technology, vital for aerospace systems, with considerable potential for further advancements in the state of the art to meet systems requirements.

##### 3.1.2 Background

Structural adhesive bonding has been used by the aerospace industry for over 25 years. Adhesive bonding provides structures having lighter weight, more fatigue resistance, and better aerodynamic smoothness than riveted structures. A good illustration of these virtues is honeycomb core sandwich construction. Other constructions, such as those described in Chapter 8 also have been used extensively, and have already proved their merit during years of service and will undoubtedly be used in future aerospace vehicles. Adhesives of the types described in Chapter 4, Section 2, also will be used in future aerospace vehicles. However, advances are needed in adhesive bonding technology to meet new systems performance requirements; to be compatible with recent advances in structural materials technology and design concepts; and to decrease manufacturing and maintenance costs. For example, new systems will further emphasize durability and reliability in addition to high strength. The recent development of boron fiber and

graphite fiber composites will require development of adhesive bonding technology that is more compatible with these materials. New, more automated, manufacturing techniques with attendant lower labor costs and with "built-in" inspectability will be necessary.

### **3.2      Current Bonding Applications**

#### **3.2.1    Current Aircraft Bonding Applications**

This subdivision will concentrate on aircraft applications that are primarily of direct interest to the government services. However, much of the current adhesive technology is used in civil aviation and many of the future developments also are expected to be applicable.

The Department of Defense services have long been deeply involved in developing aeronautical technology and thus have a history of development of and utilization of adhesive bonding as a joining technique for aircraft, missiles, and space vehicles. On the other hand, the National Aeronautics and Space Administration (NASA) only recently has changed its emphasis from a predominance of space activities to a more uniform balance between space and aeronautics. This change is in keeping with a general recognition by the governmental services of the importance of aviation, both civilian and military, to the nation's technical and economic world leadership.

##### **3.2.1.1   Fixed Wing Aircraft**

The development of the honeycomb core sandwich concept has provided the greatest impetus to date for adhesive bonding in aircraft construction. The major applications to fixed wing aircraft have been in the following areas:

- a. Control surfaces, such as ailerons and flaps
- b. Empennage (horizontal stabilizer, rudder, vertical fin)
- c. Skin panels for wings and fuselage
- d. Miscellaneous, such as engines, radomes, and secondary structural applications (fairings, flooring, etc.)

Control surfaces have been fabricated primarily as aluminum skins bonded to aluminum honeycomb and aluminum "closeout"\* members in a full-depth honeycomb construction.

Two basic types of construction have been used in the empennage area. One type involves aluminum skins bonded to a substructure, consisting of full-depth aluminum honeycomb core with interspersed spars and ribs, at the perimeter to closeout members. The other type is the non-sandwich spar-rib construction in which aluminum skins are bonded to the spars, ribs, and closeout members.

Skin sandwich panels are generally thin (i. e. , less than 1 inch thick) and are generally composed of aluminum skin bonded to aluminum honeycomb core. The inner and outer skins are usually bonded together at the perimeter to form a closeout portion and are attached with mechanical fasteners through the closeout to structural framework.

A complete listing of military aircraft employing adhesive bonding in the above types of airframe construction would be inappropriate, but among those which can be cited are the Air Force's F-111 and F-15 and the Navy F-4 fighter-interceptor and the F-14 carrier-based fighter. While the initial bonding requirements in military aircraft were primarily for metal-to-metal bonding, the advent of advanced composites has introduced a new dimension to aircraft adhesive-bonded applications. For example, the Air Force F-15 fighter utilizes a skin of boron-fiber-reinforced epoxy for the horizontal stabilizer in place of aluminum skin.

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\* "Closeout" members, employed frequently in airframe construction, can be of many types (see MIL-HDBK-23, Part 1, pp. 70-72, October 5, 1959) however, a general description of a closeout member is that it is a means of "closing-out" or smoothing out the otherwise irregular edges or other discontinuities of a sandwich panel. Sometimes this can be achieved by bonding an extra member to the panel, but the use of a design approach such that the original sandwich material closes up the discontinuity (e. g. , crushing the edges of the sandwich panel together) also is employed. These closeout members thus can function to seal the structure against the ingress of moisture or other contaminants and to facilitate the transfer of loads.

Miscellaneous applications for adhesive bonding include those associated with sandwich radomes, where glass-fiber-reinforced plastic skins must be bonded to glass-fiber-reinforced plastic honeycomb. Adhesives for such use must be compatible with radar transmission requirements and therefore may be formulated somewhat differently (e.g., no metal filler) from adhesives used for metal-to-metal bonding. Secondary structural applications such as fairings and floorings for cargo decks have been used frequently. The applications of bonding to engine structures are not yet numerous, but the bonding of titanium skin to an aluminum honeycomb core sandwich in the inlet of the engine of the Navy F-14 fighter is one example.

Despite the advantages of adhesive bonding mentioned in Section 3.1.2 there are some problem areas serious enough to force designers to be reluctant to specify adhesive-bonded construction. One of the most serious of these problems is moisture-induced failure. For example, experience with the Navy F-4 in Southeast Asia has demonstrated that bonded sandwich panels are susceptible to attack by moisture, leading to water entry and extensive bond line corrosion, especially in the metal-to-metal area. The most susceptible areas are the bond line edges in the fastener holes, especially those containing steel bolts. Leading edges and natural drainage spots, such as the bottom edge of the vertical stabilizer, also are frequently attacked. Core-to-skin bonds are affected only after extensive leakage occurs due to edge closure debonding. The type of failure observed probably can be attributed at least in part to galvanic corrosion, resulting from the use of clad aluminum in the bond line. Navy aircraft are especially susceptible to corrosive attack because of their exposure to sea water, salt spray, etc.

The problem is further aggravated by the fact that bonded structures are difficult and expensive to repair. The adhesives used in the original construction are usually high-temperature-curing resins (e.g., 120 to 170°C). (Room temperature curing adhesives are available, but they are not as strong as desired and they do not have a sufficiently high heat-distortion temperature to be used in critical applications on high-performance aircraft.) However, it is seldom possible to use

high-temperature-curing adhesives in on-site repairs so the repair facility must either replace large sections of wing, fuselage, or engine structure or "make-do" with the low-performance, low-temperature-curing adhesives.

The government services have emphasized the development of new improved adhesives and adherend surface treatments and more efficient, low-cost bonding processes relating to new methods of airframe construction. Foremost among these new methods has been the development of engineering approaches for efficient, economical utilization of composite materials in aerospace structures. While most of the attention of the airframe companies and some DOD agencies has been directed toward "all composite" structures, the NASA has been strong in promoting the concept of selective reinforcement of metallic structures with filamentary composite materials (Brooks et al. 1972), quite often in cooperative projects with military services. This concept involves bonding an overlay of one or more plies of composite such as boron-epoxy or graphite-epoxy to a metal structure. The resin matrix in the composite prepreg may serve as the adhesive if it has satisfactory rheological and adhesive characteristics, or a separate adhesive may be used. This hybrid design is considered by some to be an evolutionary approach to the all-composite structure. Although there may be an initial reluctance by designers to depend solely on bonding as the means of attaching the composite to the metallic structure, complete reliance on bonding should be the goal.

A current application for adhesive-bonded composites in selectivity reinforced metallic aircraft structures is reinforcing the center wing box of C-130 aircraft. A number of these transport airplanes have experienced fatigue damage in U.S. Air Force (USAF) service; consequently, some have been retrofitted with a strengthened aluminum center wing box to alleviate the fatigue problems. However, a study (Petit 1970) disclosed that in place of the strengthened aluminum box, 230 kilograms of boron-epoxy composite bonded to the skin and stringers of the 11-meter long box could reduce the stress levels and thus increase the fatigue life as well as does the strengthened aluminum design, but at a 13 percent saving in weight. The joint NASA/ USAF program involves the ground testing of one such wing

box in 1973 and flight service for two installed wing boxes in 1974. Bonding of the boron-epoxy composites will be accomplished with a 105°C-cured epoxy adhesive.

In addition to applications based on selective reinforcement with composites, a NASA-sponsored application of adhesive bonding to aircraft structures for the purpose of developing confidence in composites under flight service conditions involves a composite honeycomb material (Lockheed 1973). This utilizes wing fairings with PRD-49/epoxy skins bonded to a Nomex\* honeycomb core. Bonding of the composite skin is accomplished with a 105°C curing epoxy, although in regions exposed to engine heat an epoxy bonded at 175°C is used. That adhesive bonding in such airframes has a long way to go is reflected by the traditional mechanical fastening used for attachment of the fairings.

Perhaps the most extensive flight service program sponsored by the NASA involving the applications to composites is the B-737 spoiler program scheduled for implementation in 1973. Secondary bonding of graphite/epoxy skins to aluminum cores, as well as bonding to aluminum "closeout" spars and fiberglass-epoxy ribs will be accomplished with a 105°C curing epoxy. This use of bonding will be an extensive one, since over 100 such spoilers will be fabricated, tested, and applied in flight service. Thus, a statistically meaningful evaluation of performance will be possible.

#### 3.2.1.2 Rotary Wing Aircraft

Adhesive bonding is used extensively by all three military services in the construction of their helicopters. The U.S. Army, in particular, considers the current helicopters to be easily the largest application of this joining technique in terms of critical or primary structural applications.

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\* PRD-49 (new name is Kevlar [Aramid]) is a tough polymeric, highly aromatic polyamide fiber used as reinforcement in composites. Nomex is a polymeric polyamide fiber used in a variety of applications involving honeycomb. Nomex is also classed as an aramid. Both are duPont products.

One of the most demanding uses for adhesive bonding in helicopters is in the rotor blades. The construction of main rotor blades usually consists of aluminum-, titanium-, or glass-fiber-reinforced plastic skins (according to strength and service temperature requirements) bonded to metal ribs in the forward section and to honeycomb core to form the trailing edges. Among the classes of helicopter utilizing this type of construction are the Army CH-47 Chinook, UH-1 Iroquois, AH-1 Cobra, CH-54 TARHE, and OH-6 Cayuse; the Navy CH-46A and UH-46A Sea Knight, and the Air Force UH-1N, CH-3, and CH-53. The tensile and shearing forces to which the main rotors are subjected are relatively large; yet the adhesive systems have generally proved reliable.

In addition to the bonding of main rotors, tail rotor blades and floor beams of helicopters utilize adhesive bonding. Among the secondary structures making use of bonding technology are honeycomb-based floor panels, engine and transmission decks, bulkheads, cabin top work decks, and tunnel covers. The selective stiffening of skins and other components in areas of increased stress and mechanical fasteners involves the use of adhesives.

A prime example of selective reinforcement to service aircraft has been one sponsored by the NASA Langley Research Center for use on a CH-54B helicopter. During developmental flights, certain lifting configurations led to unfavorable dynamic conditions requiring more vertical bending stiffness in the 6-meter long aft fuselage (tail cone). Because the resulting production design required heavy top and bottom aluminum skins, causing the aft fuselage to weigh 175 kilograms, the manufacturer, working on a joint NASA/USA program, designed and built a tail cone with thinner top and bottom skins (Weige 1971). These skins were adequate for static-strength requirements; boron-epoxy strips then were bonded to the stringers in sufficient quantity to meet the additional requirements for vertical bending stiffness under dynamic response conditions. This reinforced tail cone, weighing 118 kilograms (a 30 percent weight saving), was installed in a helicopter experiencing routine flight service. The initial 200 hours of flight service disclosed no evidence of failure in the bonded composite.



In spite of generally favorable experience, some problems have been experienced with bonded segments of Army helicopters and fixed-wing aircraft (see references 11, 12, 13). In general, the incompatibility of the chosen materials of construction and the processes chosen for production have been highlighted as major contributors to some early bond failures. The synergistic effects of humidity and elevated temperature also have given rise to failure of bonded segments. Improved adhesives, primers, and surface preparations that promise solution to some of these problems have been developed.

### 3.2.2 Current Spacecraft Bonding Applications

Adhesives have been used widely in spacecraft applications. In manned and unmanned spacecraft, they have proven useful, particularly in view of weight-saving considerations, for bonding both primary and secondary structures. Since the materials chosen for spacecraft structures are usually the lightest possible for the job, adhesive bonding is chosen not only as the lightest joining technique but also because the lightweight materials preclude use of traditional joining methods, such as welding, mechanical fastening, etc. Moreover, the same materials are not always the best for each component; adhesive bonding becomes the preferred joining method for dissimilar parts. Sandwich constructions are ideal for many applications due to their inherent stiffness and light weight; thus, adhesives find numerous applications in the manufacture and use of sandwich components.

The requirements for adhesive bonding on spacecraft often are extremely stringent because of expected exposure to the unique feature of the space environment and launch (e.g., high vacuum, shock, extremes of temperature, and radiation). The use of plasticizers or other volatile components in adhesives can be undesirable, not only because of the effects of the space environment on adhesive mechanical properties but also because transport and deposition of the volatile species from warm sites to cooler sites can lead to contamination of optical and electrical components. The thermal requirements for using adhesives can range from  $-185$  to  $121^{\circ}\text{C}$ , the cold extreme being the more hazardous; the cycling of the temperature between

extremes in spacecraft operation is also important. Many current adhesives are able to withstand the effects of particulate radiation, although certain orbits, such as those within the Van Allen belt, and long interplanetary mission times could result in adhesive deterioration. Ultraviolet radiation is a matter of concern for certain external applications. The static and dynamic loads encountered by a spacecraft during launch, such as axial compression and bending and vibration-induced loads, lead to mechanical stresses that must be anticipated in adhesive designs.

High reliability is essential to the use of adhesives in spacecraft since the slightest malfunction or failure, once the craft is in orbit, can seriously jeopardize the performance of the mission. The reliability required can be accomplished by rigid quality control of the materials and fabrication processes, together with adequate inspection and testing procedures. However, conditions occur which can be neither anticipated nor simulated.

#### 3.2.2.1 Manned Spacecraft

All of this country's manned spacecraft--Apollo, Gemini, and Mercury--have used adhesives extensively. For example, in Apollo (Epstein 1971) honeycomb sandwich construction is used widely where aerodynamics loads are encountered. The command module was a leak-tight aluminum-honeycomb conical structure using aluminum sheets bonded to aluminum honeycomb core with an epoxy-phenolic adhesive. A large number of details were bonded to this structure using epoxy-based adhesives to preserve the leak-tight system. Flammability and toxicity of the adhesives were major concerns in pressurized manned areas of Apollo. The command module employed a heat shield consisting of epoxy novolac-phenolic ablator in a glass-reinforced honeycomb core, the system being bonded to a stainless steel sandwich honeycomb substructure with an epoxy-phenolic adhesive.

The Apollo service module had a sandwich structure of aluminum skins and honeycomb bonded together with epoxy-phenolic tape adhesive. In addition, aluminum radiator panels were mounted by adhesively bonded phenolic-glass honeycomb sandwich panels, which were bonded to the outer skins. The lunar

module and its spacecraft adapter used adhesives extensively, not only in sandwich construction applications, but also as seals for mechanical fasteners and seams (epoxy-based adhesive) and as skins for securing various aluminum clamps and brackets.

Numerous adhesives were used in the Saturn S-II launch vehicle. Outstanding among the applications was the 33-foot diameter common bulkhead, which was perhaps the largest primary structure ever made by adhesive bonding. This structure, which separated the LOX (liquid oxygen) and LH<sub>2</sub> (liquid hydrogen) tanks, was bonded with an epoxy-phenolic adhesive because of its excellent mechanical properties at cryogenic temperatures (-253°C.)

#### 3.2.2.2 Unmanned Spacecraft

A comprehensive tabulation of unmanned spacecraft adhesive applications, listing both spacecraft types and specific applications, has been compiled, (Rittenhouse and Singletary 1968) and the intent here is to cite representative examples, not repeat the listing. Solar panels have been used in a variety of spacecraft and adhesive bonding has played an important part in their construction. In some cases, the solar panels have been built to serve not only as the panel for the solar cells but also as the primary structure of the spacecraft. In one particular communications satellite, the solar panel was a cylinder of epoxy-glass skins co-bonded to aluminum honeycomb core. All laminating and bonding operations, including the closures and core segments, were performed in one step. Independent solar panels also have been used, and thin-gauge metal skins often have been bonded to the aluminum core in place of epoxy-glass skins. When this is done, a dielectric layer must be bonded onto the exterior metal skin before attachment of the solar cells in order to provide electrical insulation. Virtually all solar panel bonding has been done with epoxy-based adhesives. Because of the unusually large solar panel area that may be needed to meet electrical power requirements, appendages of solar panels may be extended after the spacecraft has been placed into orbit. Although these have usually been built of adhesively bonded honeycomb sandwich panels, more recent

developments have been made in foldout and rollout solar arrays. One of these was a polyimide film laminated with a thin glass-epoxy layer onto which the solar cells were bonded. The resulting configuration was then rolled up for launch and unrolled after orbit.

The attachment of the solar cells to the panels in a large number of spacecraft has been extremely dependent upon practical, reliable adhesive bonding (Epstein et al. 1972). Thousands of solar cells must be mounted to provide a satellite's electrical power, and these silicon solar cells, usually 2 centimeters square, must have a protective thin quartz solar cell cover bonded to the solar cell. Nonaromatic RTV silicones (polydimethylsiloxanes) have been generally used. Quality control of these adhesives has had to be rigid to minimize UV degradation. Both epoxy-based and RTV-silicone adhesives have been used to bond the solar cells onto the solar panel structure. Low temperatures (less than  $-73^{\circ}\text{C}$ ) can lead to embrittlement; polymethylphenylsiloxanes have been preferred for use under such thermal conditions.

Somewhat related bonding requirements have been encountered for second-surface mirrors that serve to maintain a narrow range of spacecraft temperature. However, in contrast to solar cell panels, second-surface mirrors often operate at temperatures as low as  $-129$  to  $-189^{\circ}\text{C}$ . and often for long mission lives. These mirrors are constructed by bonding thin, fragile glass or quartz plates, metallized on the back face, onto the spacecraft. Thermal control is achieved as a result of the low solar absorptance of the highly reflective metallic substrate and the high emittance of heat from the thin transparent cover glass. Various RTV-silicones have been the adhesives of choice in most applications. Reflective radiation surfaces also have been adhesively bonded to the exterior of the spacecraft as another form of thermal control.

Among the many other ways in which adhesive bonding plays an important part in the fabrication and operation of unmanned spacecraft are multilayer circuit boards, antenna reflectors, various tubular truss configurations adhesively bonded for assembly purposes, and panels for the mounting of

equipment. And last, but by no means least, must be mentioned the vital function of adhesive bonding of reentry heat shields. The heat shield of a representative recoverable spacecraft uses a glass-phenolic honeycomb sandwich substrate as the load-bearing structure. A glass phenolic honeycomb core is then bonded, with a heat-resistant epoxy-phenolic tape adhesive, onto the substructure. This honeycomb is then filled with the ablative insulation material, such as RTV-silicone elastomers or epoxies.

### 3.2.3 Current Missile Bonding Applications

#### 3.2.3.1 Tactical Missiles

The military services have relied heavily upon adhesive bonding in the fabrication of tactical missiles. In the 1950s the Army was using adhesive bonding in missile systems, and the applications involved both primary and secondary structures. Warheads such as the M17 and the M155 for the Nike Hercules and Hawk, respectively, were assembled from component parts by structural adhesive bonding. Main supports and ablative shields for the warheads depend upon adhesive bonds. Current missiles, such as the improved Hawk, utilize adhesives in warhead and vehicle components. Honeycomb sandwich constructions for wings, motor liners, and motor nozzle liners are typical applications for these systems. The Lance missile system utilizes skins of aluminum-phenolic-paper honeycomb and bonded cork-silicone ablative shielding. The small missiles of the Army arsenal, such as TOW which may be fired from helicopters, also contain bonded segments in both warhead and vehicle components.

Some problems were encountered in using adhesives. These generally were associated with the newness of the technology to the contractors and as experience was accumulated in the various contractor plants and facilities were improved, quality production was obtained. Most missile systems enjoy a rather pampered atmosphere in well-cushioned containers until use; thus, the problem of adhesive joint degradations from exposure to hot, moist environments is greatly reduced. Also, since the missile has only one mission, design philosophy can differ markedly from that for helicopters in regard to structural requirements

for adhesive joints.

### **3.2.3.2 Strategic Missiles**

Adhesive bonding also has been extremely useful in the manufacture of strategic missiles. The Navy Polaris A-2 and A-3 and Poseidon C-3 vehicles have had bonding used in the construction of the outer shell and the internal structure members of the reentry vehicle. Even for such Navy missiles, the requirements on the adhesives are somewhat less demanding than those for aircraft applications. The moisture level during storage is no greater than 50 percent relative humidity and the temperature is less than 27 °C. Even during flight, the short-term exposure to water and high temperature can be tolerated by state-of-the-art adhesive resins. However, bond degradation has been reported for missiles in storage, possibly because of the aging of the adhesive or because of a brief, inadvertent exposure to high moisture levels.

In addition to bonding applications involving the structural shells of ballistic missiles, adhesives have proved useful for bonding the rocket nozzles of solid propellant rocket boosters to the structural shell or housing for the nozzle.

In order to emphasize the importance of adhesive research and development to the Defense Nuclear Agency, the following example of adhesive bonding as a means of attaching the heat shields to the substructures of strategic ballistic missiles is presented.

A concept of using adhesive bonding to achieve the most efficient use of low-ductility substructures in reentry vehicles (RV) has been proposed. Since reentry vehicles must be resistant to nuclear effects, or "hardened," materials used in their construction must be selected with care. Beryllium has been considered an important candidate substructure material for various bonded heat shields on reentry vehicles because of its low atomic number, light weight, and high stiffness and strength at elevated temperatures. Unfortunately, certain grades of high-purity beryllium can tolerate only low strains (as low as 0.3%) without failing when subjected to the multi-axial, dynamic stress states that

RVs would experience during nuclear encounters. However, the use of appropriate bonding materials for attachment of the heat shield materials was considered an attractive way to get the most out of beryllium substructures.

This proposed application of adhesive bonding imposes stringent requirements upon the bond materials. One of the most severe requirements is the ability of bonds to endure interface temperatures as high as 538° C. without degradative outgassing that would lead to pressure buildup in the bond and subsequent loss of the heat shield. The thermal limitations of conventional bond materials also can make them unsuitable for "hardened" vehicle designs if they have relatively higher X-ray absorption properties than the heat shield and substructure. Furthermore, low adhesive and cohesive bond strengths can result in the bond being the weakest link in the entire reentry vehicle during either the stress wave propagation from nuclear encounters or the dynamic structural response of the RV caused by the blowoff pressures from nuclear effects. Even if the bond itself survives, improper choice of the bond material can lead to spall (the loss of sizeable chips or fragments) or structural failure of the low-ductility substructure during these nuclear effects.

The major requirements\*imposed on bond selection by the use of beryllium or other low-ductility substructures in "hardened" reentry vehicle constructions result in the following summary of desired properties of the adhesive bond:

- a. High thermal degradation temperature (not significant outgassing to 527°C)
- b. Low absorption of X-rays
- c. High adhesive and cohesive strengths (resistance to spall and debonding)
- d. Good resistance to shock (shock-impedance values less than  $0.025 \text{ g/cm}^2\text{-microsecond}$ )
- e. A low elastic modulus ( $\sim 100 - 2500 \text{ psi}$ ) in the plane of the strain
- f. High strain values (50-75%) required before the bond "bottoms out"; that is, the bond should remain linearly

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\* See Section 3.6 for detailed analysis of requirements.

elastic in its stress-strain behavior during structural response

Specific ranges of values of these desired properties are dependent upon a variety of factors such as the heat shield and substructure materials, the configuration geometry of the reentry vehicle, and the RV systems performance requirements. The desired property values are determined through analytical studies. An example of the type of analytical study is one which, together with experimental results, has shown that "soft" or ductile adhesive bonding might be used to increase the resistance to nuclear effects, in the sense of dynamic response of bonded high-stiffness heat shield low-ductility substructure RVs. Conventional bond materials, such as epoxies, have low "bottoming" strains; that is, they become brittle at very low strain values. On the other hand, "soft" bond materials such as silicones and rubber-based adhesives, have much greater strain capability. A limited analytical study of available soft bonds indicates that they exhibit non-linear stress-strain behavior with increasing stiffness at increasing loads. The analysis also has shown that, if current soft bond materials and current concepts are to be used successfully, relatively thick bond lines are required. Therefore, it becomes a matter of whether the use of a sufficiently thick bond line to prevent the bond from bottoming out or becoming inelastic during a dynamic-response to a nuclear encounter also will result in loss of the weight advantage of the soft bond concept. Yet to be investigated are new soft bond materials that could have much higher bottoming strains compared to current soft bond adhesives, as well as bond materials with other types of nonlinear stress-strain behavior, such as materials like rubber honeycombs, which crush elastically and display decreasing stiffness with increasing strain prior to bottoming.

### 3.3 Future Bonding Applications and Requirements

Forecasting applications for adhesive bonding in aerospace activities can be extremely risky. Not only are the aircraft and spacecraft for the next decade uncertain, but the uses of adhesives for them often emerge only as a result of bonding being the best solution to a particular joining problem rather than as a



predictable joining application. However, in other cases where the joining requirements can be precisely stated, experience can dictate the use of adhesives from the start. Thus, this section points out both fairly certain applications and predictable requirements that might lead to end uses for adhesives.

### 3.3.1 Future Aircraft Bonding Applications

The utility and versatility of adhesive bonding in many facets of aircraft manufacture have been amply demonstrated, despite the fact that the decision to use adhesives often was one of last resort. Indeed, the present attitude of many aircraft designers is still one of extreme (and perhaps undue) caution. With a gradually evolving approach of designing to utilize adhesive bonding to its best advantage, and for the unique properties that can be realized, a steady growth of this joining technique is likely. However, until problems associated with such shortcomings as stress-corrosion failure, on-site repair difficulties, etc., are solved or minimized, designers probably will continue to combine conventional riveting and adhesive bonding in order to ensure joint reliability and still retain some of the advantages of adhesives. For the same reasons weldbonding is an attractive compromise.

This conservative attitude probably will prevail until the various problem areas are eliminated or diminished significantly through new developments in adhesive resins, adherend surface preparation, and joint design. However, it is possible that some of the flight service programs described in Section 3.2.1.1 will succeed in increasing the confidence level for the use of adhesives bonding.

Among the new future applications of adhesive bonding structures are the use of highly loaded laminated titanium structures, laminated by adhesive bonding, as wing carry-through members; weldbonded sheet stringer fuselage construction, and adhesive bonded static and rotating components in turbojet engines. The anticipated increased use of advanced composites in production structures can be expected to lead to increased use of adhesive bonding for joining composites to themselves and to metals. Typical applications of composites anticipated for airframe construction include advanced composite spar caps adhesively

bonded to spar webs, advanced composites bonded as overlays over metal wing skins, and bonded advanced composite parts in engines, plus the conventional applications such as honeycomb core sandwich construction.

Selective reinforcement of metallic aircraft structures and the eventual replacement of that concept by all-composite parts will continue to require adhesive bonding. Feasibility studies (Bryson and McCarty 1972; Johnson and June 1972) have demonstrated additional payoffs for selective reinforcement with composites in such applications as reinforcing the shear critical window area of a commercial transport, as well as other fuselage panels and wing components. Adhesive bonding is an essential technology to successful implementation of these composite plans. Several problems encountered in using adhesives in selective reinforcement will require a great deal of development to optimize the use of adhesives. Perhaps the most immediate problem is that of the mismatch of the thermal expansion coefficients of the adhesive and various adherends. For subsonic commercial aircraft, a thermal environment range of about  $-54$  to  $71^{\circ}\text{C}$ . is considered normal. Any use of adhesives requiring curing temperatures above that range result in considerable residual thermal stresses in the bond, stresses that can lead to distortion of the bonded materials or even bond failure. Efficient adhesives cured at about room temperature, with properties and environmental durability equivalent to thermally cured adhesives, are urgently needed to minimize the thermal expansion mismatch that results at either end of the thermal spectrum, to say nothing of the room-temperature curing adhesives so much desired by the airframe manufacturers to eliminate autoclaving operations. Such room-temperature curing formulations will be equally necessary for use in load transfer joints, the design of which has and will continue to receive much attention in order to advance the level of performance required for maximum utilization of composites in aircraft structures.

Although there may be some question about when supersonic transports will be built in the United States, few would doubt that such a time will come, and so the technology for such aircraft must be developed. Numerous studies have

left little doubt that adhesive bonding could play a major role in supersonic aircraft manufacture. Present uncertainties include whether the structure would be virtually all-titanium or would utilize substantial amounts of composites, but adhesive bonding could be used extensively in either case. Should the aircraft be Mach 2-2.5, existing adhesive systems might be adequate for most bonding needs or require only minor upgrading to meet requirements such as 204 to 232°C resistance for short periods of time. However, a Mach 2.5-3 design would necessitate new adhesive resins in order to endure 232 to 316°C for extended time periods.

Beyond the supersonic aircraft needs, the NASA envisions (Anderson and Kelley 1971) hypersonic (flight in excess of five times the speed of sound) air transports (HST) for long hauls ranging upwards from 6,000 miles. Although commercial versions of such aircraft are probably 25 years off, experimental versions could evolve much sooner. The environment associated with the predicted Mach 5-8 design probably will be the most severe to be encountered by aircraft in the foreseeable future. An adhesive system would probably be required for bonding the necessary insulation onto cryogenic tanks for the liquid hydrogen fuel. This would mean retention of adhesive properties ranging from -253 to 316°C. Panels actively cooled with liquid hydrogen also would require adhesives suitable for metal bonding. Ceramic-based adhesive systems could be required for bonding hot surface insulation into the interior of engines that, although actively cooled with hydrogen, still would experience temperatures up to 1093°C. Such a radical high-performance aircraft clearly suggests that there is no limit to the extent of improvement in adhesive bonding that would be desired.

The military services will continue to use adhesive bonding for helicopters. Such applications as all-reinforced plastic rotor blades (utilizing adhesive bonding) with leading edges of titanium for combined erosion protection and stiffening provide significant increases in helicopter performance. Improved lightweight fuselage segments for helicopter gun ships that serve dual roles as structural components and armor will place adhesives in a new role. Shafts for power transmission to rotors will be improved and reduced in weight by utilizing composite materials with

bonded end couplings. Elastomeric shock absorbers or vibration dampers will be incorporated in the composite shafts to reduce bearing problems; these elastomeric segments will be bonded in place.

### 3.3.2 Future Spacecraft Bonding Applications

The uncertainty of manned space exploration during the next decade is balanced by the reasonable certainty of the space shuttle program and the continuing use of unmanned space vehicles. The requirements for adhesives during this next decade can be exemplified by the needs for the space shuttle. This spacecraft, shaping up as the main NASA-sponsored vehicle during the 1970s will probably utilize adhesive bonding in a number of ways. Among the proposed thermal protection systems is one that would use a compacted reusable surface insulation (CRSI), such as mullite. CRSI panels would require bonding to a chemically-blown pad of foamed silicone elastomer, thus giving strain isolation of the CRSI from the aluminum structure. The thermal requirements would range from 343°C for the outer surface of the foam pad to 177°C for the inner surface (foam to aluminum), with -113°C as the lowest temperature expected. Silicone adhesives have been proposed for both pad and panel bonding, but 343°C could be excessive for them. Certainly this emphasizes the need for an elastomeric adhesive with a 30 to 55°C advantage over state-of-the-art adhesives. It has been predicted that about half a ton of adhesive, representing 6 percent of the weight of the CRSI thermal protection system, would be used. A reduction in the bonding weight would seem to be in order.

Other adhesive requirements expected for the space shuttle would be those to meet applications requiring thermal durability from as low as -253°C (liquid hydrogen) without embrittlement of the adhesive bond, and up to from 316 to 343°C. The applications would involve bonding of various types of composites, including glass/epoxy, glass/polyimide, graphite/polyimide, and organic fiber/epoxy to each other and to aluminum and titanium.

For a variety of types of future spacecraft, high-modulus graphite-fiber-reinforced plastics can be expected to be used extensively as skins in sandwich

structures and in shell and truss type structural elements. The principal reasons for this are that graphite-fiber-reinforced laminates can be designed to have a coefficient of thermal expansion (in-plane) of nominally zero, in addition to having high modulus-to-density and strength-to-density ratios. These combined attributes make this material very attractive and cost effective for applications such as microwave antenna reflectors and structural substrates for mirrors, as well as for use in the main spacecraft structure.

The use of adhesives in second-surface mirror coatings for thermal control of spacecraft was mentioned in Section 3.2.2 of this chapter. A need for improved adhesives for such applications, particularly in the assembly of flexible second-surface mirror coatings, will continue. A flexible second-surface mirror is a modification of the rigid variety that uses metallized glass or quartz plates and involves the use of transparent polymeric film (such as FEP Teflon) that has a mirrored metal surface, such as silver or aluminum, deposited on one side of the film. The flexible mirrored film then is adhesively bonded to the spacecraft structure. The principal limiting requirements for such an adhesive are those associated with the vacuum of the space environment: It should be virtually free of outgassing tendencies that could result in bubbles or rupture defects in the metallized polymer coating. More specifically, general requirements of less than 1 weight percent volatiles and less than 0.1 percent condensibles at 125°C in a vacuum of  $10^{-7}$  torr have been cited for such adhesives. State-of-the-art polyurethanes, silicones, and acrylics do not meet such conditions. In another form of flexible second-surface mirror coating (still in the conceptual stage), a very thin second polymer film is laminated onto the polymer surface of the metallized film that is exposed to the space environment. The thin laminated polymer functions to screen out radiation, such as high-energy particulate (solar wind plasma) and ultraviolet, that would damage the primary coating film. In order to accomplish the lamination of the screening film, an adhesive is required that not only will meet the above vacuum compatibility requirements but also will resist any penetrating radiation without significant change in its optical characteristics. The

above restrictions generally would satisfy the requirements for normal spacecraft in earth orbit or on a lunar interplanetary mission. In addition to the above space environmental constraints, the method of applying such materials should be considered. The bonding of the entire flexible second-surface mirror coating might best be accomplished by means of a pressure-sensitive adhesive, perhaps double-backed onto a thin polymeric film. The material should be amenable to application over large areas, and it should be readily removed and replaced, in small sections, for repair of damaged portions.

General or miscellaneous applications for adhesives can be expected to continue in the future. However, resistance to more severe space environmental conditions for much longer periods of time will be needed for interplanetary exploration. Unmanned near-sun missions will require adhesives that retain their integrity under rapid temperature cycling (from perhaps 260 to  $-73.3^{\circ}\text{C}$  for a Mercury flyby) at high vacuum. A relatively high exposure to high-energy protons and electrons would be expected. Research to date (Roper 1971) has suggested that adhesives based on aromatic-heterocyclic polymers (polyimides, polybenzimidazoles, polyquinoxalines, etc.) have the best potential for meeting these requirements. Unmanned outer planet missions, exemplified by the proposed "Grand Tour" of Jupiter, Saturn, and Pluto in the late 1980s, will require adhesive materials that will not embrittle after exposure to extreme cold ( $-225^{\circ}\text{C}$ ) for periods as long as 12 years under high vacuum. Radiation doses would be less severe than those for near-sun missions, but the length of such missions would still build up a considerable exposure to solar wind plasma.

Improved adhesives for optical applications such as for bonding windows in orbiting telescopes, etc., will continue to be needed. One of the primary needs will be for markedly improved adhesives for the bonding of solar cell components. The silicones that generally have been used are far from completely satisfactory because of their out-gassing tendencies and their darkening from ultraviolet radiation and 100 to  $150^{\circ}\text{C}$  temperature. These adhesives will need much attention over the next 5 to 10 years as solar cell technology gets close scrutiny

as a possible means to alleviate the impending world energy shortage.

### **3.3.3 Future Missile Bonding Applications**

Adhesive bonding has been firmly established as useful for both tactical and strategic missile construction. The extent of future applications undoubtedly will be influenced by experiences with current bonded components. Weldbonding is expected to become the most significant new manufacturing technique from the standpoint of generating further reliance on adhesive bonding, and it is also expected to lead to weldbonded fuselage structures for tactical missiles. The fabrication of complicated structures by adhesive bonding generally requires an equally complex array of lay-up jigs or fixtures for the accurate alignment of components. Now, however, the demonstrated practicality of combined spot welding and adhesive bonding, with or without the added use of mechanical fasteners (such as rivets), promises significant cost reduction advantages. This cost reduction would be especially effective for the small productions runs frequently encountered in missile production.

Other advanced fabrication developments appear to be imminent in missile manufacture. Composite missile skins laminated of materials chosen for certain unique properties and stiffened by corrugation and other techniques are now feasible. Brittle, strain-sensitive materials can be joined by using adhesives of graded moduli and intermediate-modulus materials. The Air Force recently has completed a development program in which adhesive bonding was used to fabricate a reinforced plastic fuselage for a tactical missile. The concept involved the fabrication of four identical longitudinal sections (quadrants) of reinforced plastic with molded fins, bonded together to form the fuselage and lifting surfaces of the missile. Demonstrated validity of this concept could pave the way for this interesting use of adhesives in production.

The possible weight and cost savings to be gained through use of adhesive bonding in the Navy Poseidon C-4 missile indicate an even greater use of adhesives than in the current C-3 model. These advantages far outweigh the aging problems noted in Section 3.2.2. However, the advanced state-of-the-art, high-strength,

high-modulus adhesive resins, which are of interest in missile design, attain these properties at a sacrifice in fracture toughness. Consequently, joints may be unexpectedly sensitive to impact, vibrational fatigue, and moisture which could affect the reliability of the structure over months or years of storage. Adhesive suppliers do not provide fracture toughness data, so even if the designer is aware of the problem he is unable to judge its severity. Fortunately, there is a growing awareness of the fracture toughness trade-off and some data now is being generated. The Navy has been concerned about this problem for some time and has supported work on test methods for determining the fracture behavior of adhesives.

The adhesive investigations by the Defense Nuclear Agency will continue to center on materials and concepts for use in nuclear-resistant reentry vehicles. The use of soft or energy-absorbing adhesive bonds to enable the reentry vehicle to resist the impulsive loads resulting from nuclear effects appears to be feasible. However, the properties of the adhesive that would be required to make the RV resistant to other aspects of nuclear effects (e.g., energy deposition) have not been defined. Similarly, the implications of use of the concept in system design and fabrication and system response have not been considered. Also, the soft bond concept has been studied analytically and experimentally only in ring configurations; its use in RV shell structure might produce responses other than those desired.

Completion of the investigations currently in progress and future investigations based on the above considerations will lead to the following state of the art for utilization of bonds for RV hardening:

- a. Specified values of desired bond properties (mechanical, thermal, and absorption)
- b. Verified analysis methods
- c. Adhesives having desired elastic moduli
- d. Solutions to potential major design problems
- e. Guidelines for applications in RV design and fabrication



In addition, it also remains necessary to pursue the development of adhesive materials sufficiently resistant to nuclear effects and to apply and test them in actual or simulated advanced RV constructions.

### **3.4 Analysis of Requirements for Adhesives to Bond Heat Shields to Reentry Vehicle Substructures**

Beryllium has been considered an important candidate substructure material for various bonded heat shields on hardened reentry vehicle constructions. Beryllium is attractive because of its low atomic number, light weight, high stiffness, and high strength at high temperatures. Unfortunately, several of the grades of high-purity beryllium, which are candidates for hardened RV applications, can tolerate only low strains (as low as 0.3%) without failing when they are subjected to the multiaxial, dynamic stress states that RVs experience during nuclear encounters. This combination of properties suggests that compatible bond and heat shield materials be utilized to achieve efficient use of beryllium substructures for hardened RVs. This imposes stringent requirements on the properties of the bond materials utilized in such construction.

The high interface temperature ( $\sim 538^{\circ}\text{C}$ ) associated with optimum beryllium substructure may be sufficient to cause bond outgassing and eventual loss of heat shield due to pressure buildup. The thermal limitations of conventional bonds also can make the bond materials the "weak links" in hardened vehicle designs against energy depositions from nuclear weapons, depending upon the relative X-ray absorption properties of the heat shield, bond, and substructure.

In addition, low bond strength can cause the bond to be the hardening weak link during the stress wave propagation (Figure 1) or the RV dynamic structural response (Figures 2 and 3) caused by blowoff pressures resulting from nuclear effects. Alternately, improper choice of the bond material can lead to spall (Figure 4) or structural failure (Figure 2) of the low-ductility substructure during such stress wave propagation or RV dynamic structural response even if the bond itself survives.

The above paragraphs justify the major requirements imposed on bond design by use of beryllium or other low-ductility substructures in hardened RV constructions. The bond properties, relative to heat shield and substructure

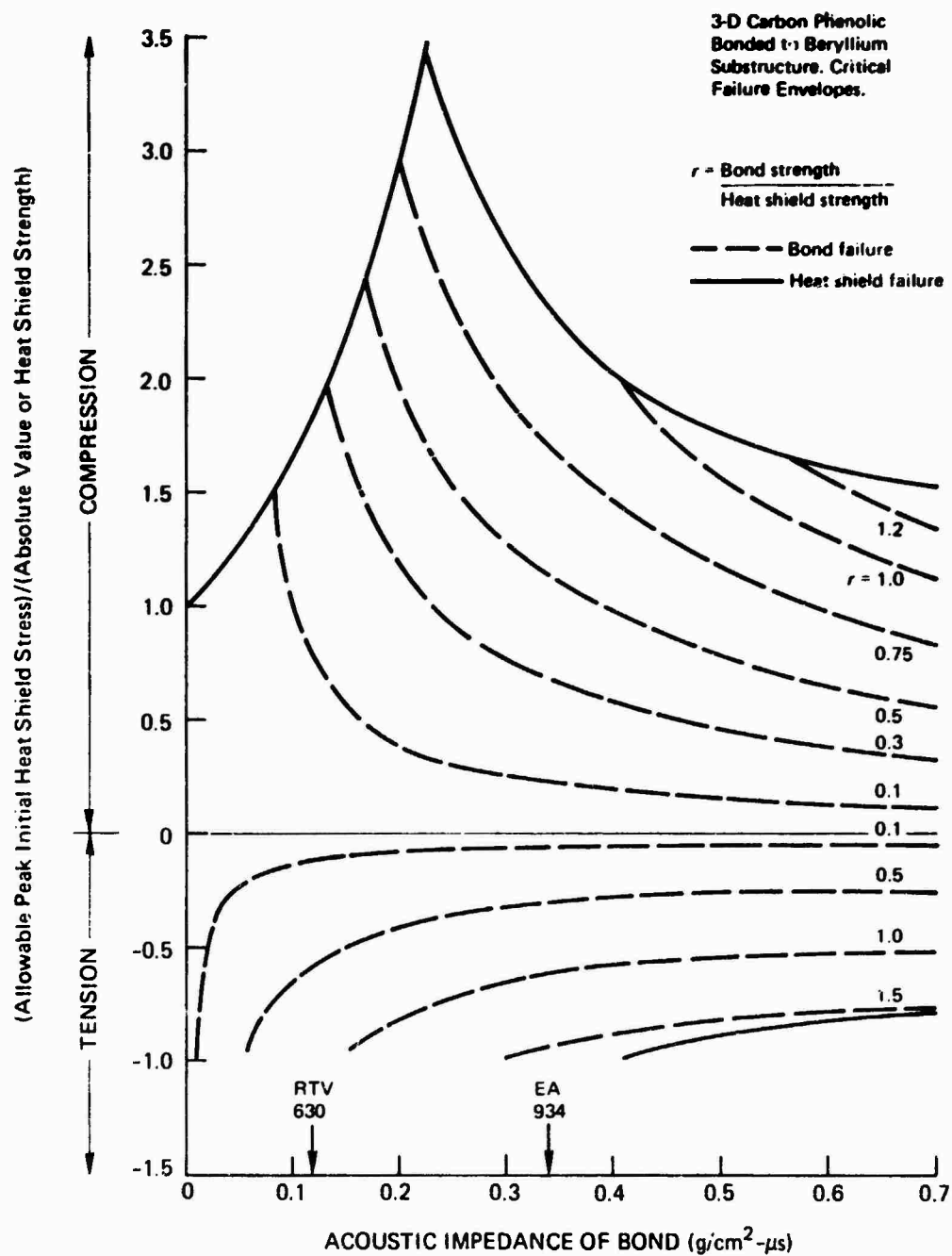


FIGURE 1 Variation with bond acoustic impedance of threshold amplitude of stress wave in heat shield for failure of bond or CP heat shield (CP/BE).

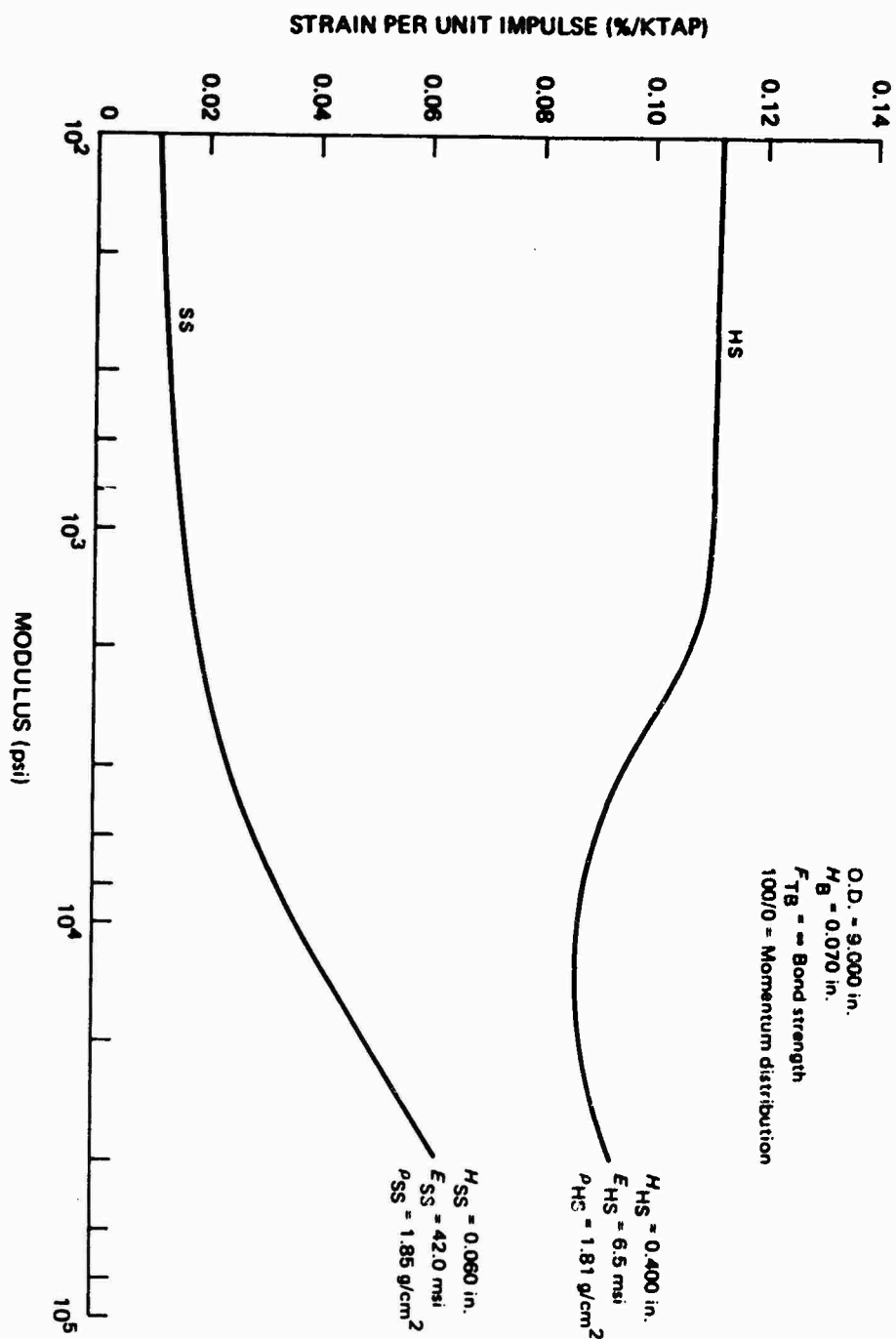


FIGURE 2 Effects of bond modulus on heat shield and substructure maximum strains.

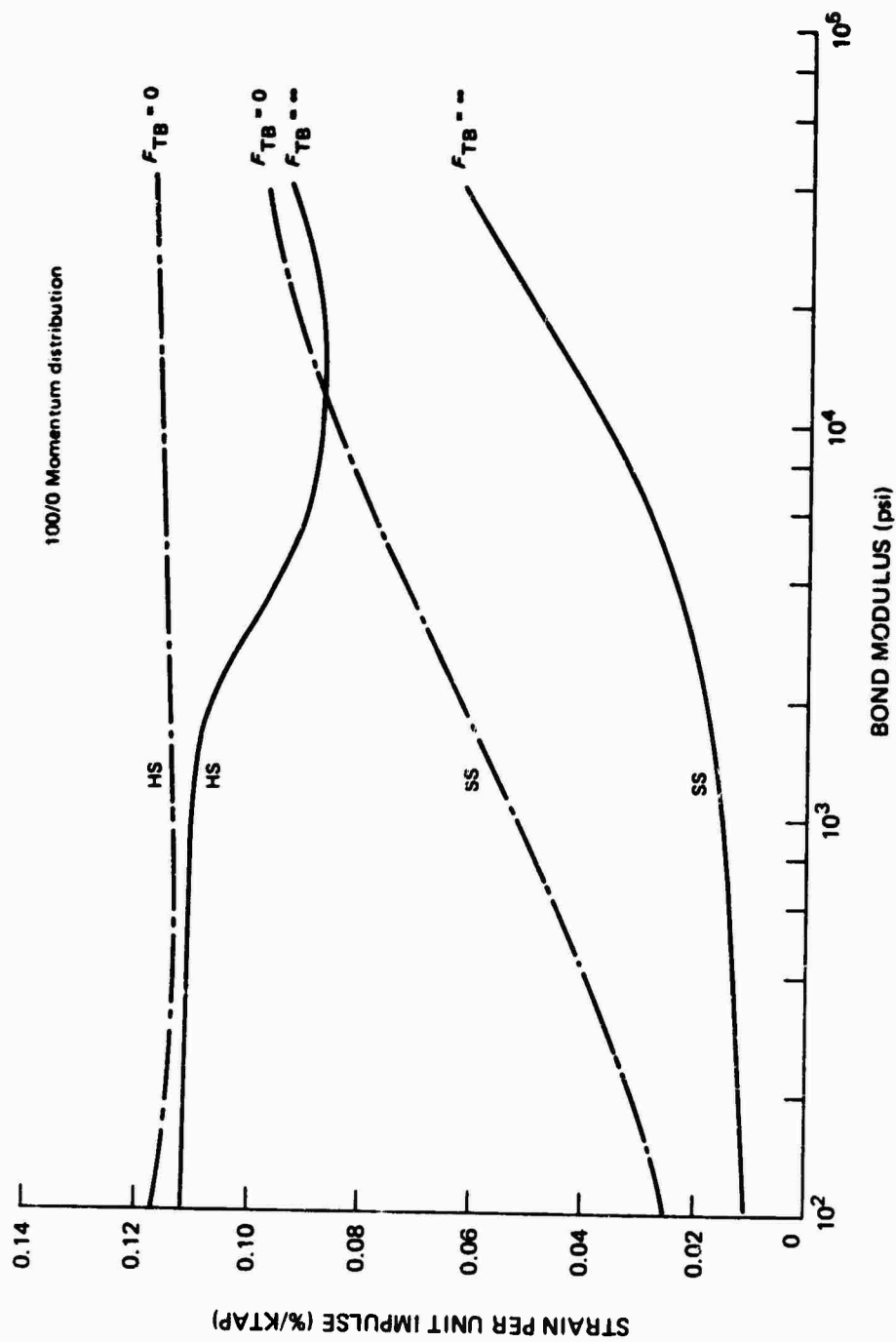


FIGURE 3 Effects of bond tensile strength  $F_{TB}$  on heat shield and substructure maximum strains.

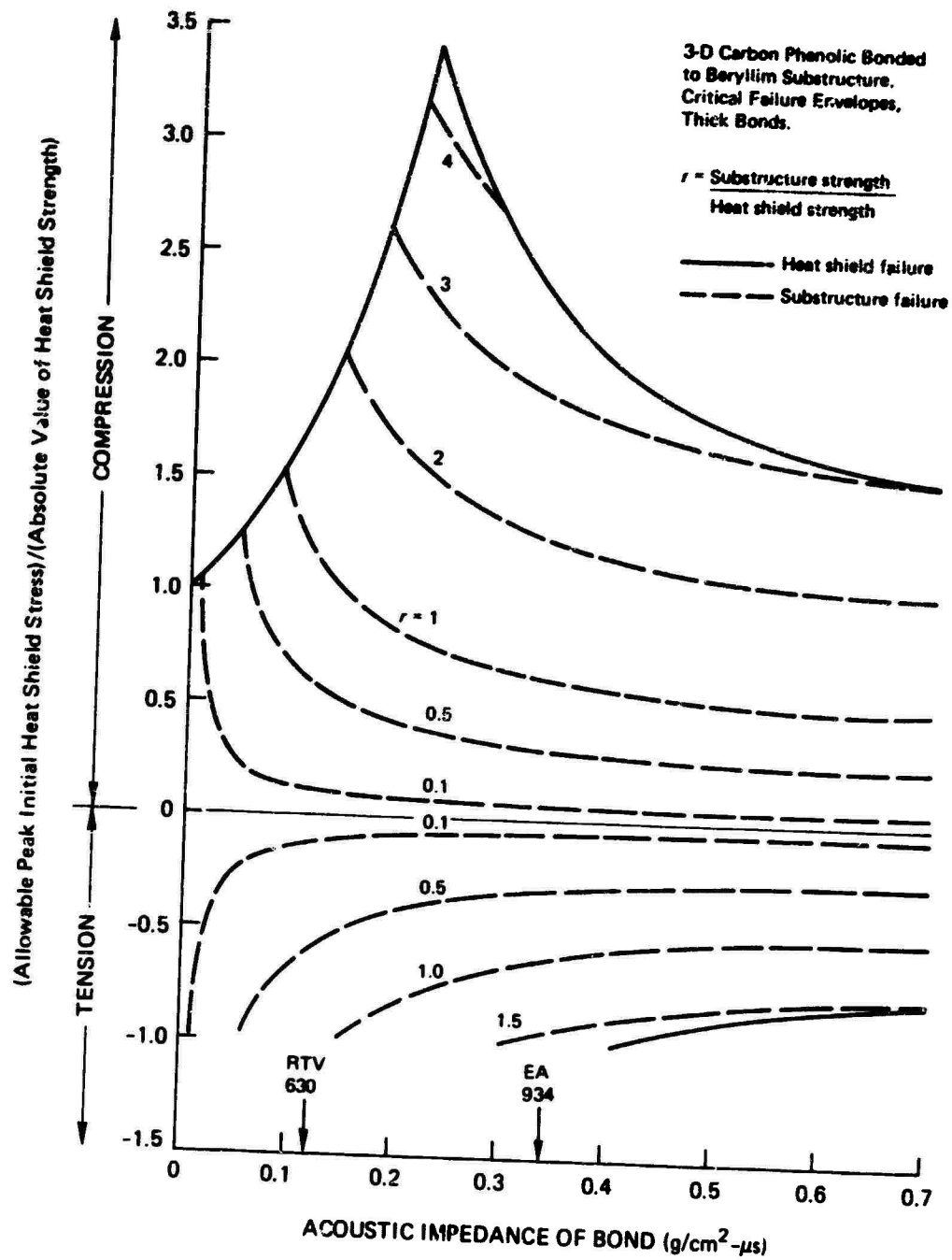


FIGURE 4 Variation with bond acoustic impedance of threshold amplitude of stress wave in heat shield for failure of BE substructure or CP heat shield (CP/BE).

properties are stated in Section 3.2.3.2.

The specific ranges of desired values of these bond properties depend on the heatshield and substructure materials, RV configuration geometry, and RV systems performance requirements. These desired property values are determined through analytical studies.

Based on the results of a preliminary study to determine the desired magnitude of the bond uniaxial strain modulus to effect increased hardness of RVs during dynamic structural response, an in-depth study is currently being conducted to investigate bond selection for RV hardening, with the following objectives:

- a. Analytically establish and experimentally verify the desired bond properties and thickness to increase response hardness levels of RV structures made of heatshield and substructure construction
- b. Establish the sensitivity of the desired values to change in heatshield and substructure mechanical properties and thicknesses.
- c. Provide guidance for material development

The studies indicate that, for certain currently desired hardness levels, the use of bonds with appropriate properties may result in adequately hardened RVs that do not require additional hardening schemes and that, therefore, suffer little or no hardening weight penalties caused by the use of bonded, limited-ductility substructures.

Analytical and experimental results indicate that soft bonds can be utilized in place of hard bonds to increase the dynamic-response hardness levels of bonded high-stiffness heat shield plus limited-ductility substructure constructions if the following conditions are met:

- a. The bond modulus is appropriately low (specific values are a function of heatshield and substructure materials and thicknesses, local vehicle diameter, and local bond line thickness)

- b. The bond remains linear elastic in its stress-strain behavior during structural response (the bond does not bottom)
- c. Bond line spall or debonding does not occur.

In order to meet the first two conditions, the analyses indicate that a relatively thick bond line is required if the soft bond materials and concepts currently available are utilized in reentry vehicle construction. Conventional bonds have relatively low bottoming strains. A limited analytical study has been conducted of bonds that exhibit nonlinear stress-strain behavior with increasing stiffness at increasing loads. This stress-strain behavior is representative of the behavior of available soft bonds. The analytical study indicated that if these bonds were permitted to bottom, an inappropriate choice of the nonlinear properties of the soft bond could cause hardness levels to decrease below levels achieved with hard bonds. However, all the parameters that represent the type of stress-strain nonlinearity described above have not yet been studied to determine acceptable bond bottoming characteristics. In addition, other types of bond nonlinearity, particularly that of decreasing stiffness under increasing strain prior to bottoming (which is exhibited by materials that crush elastically, such as rubber honeycombs), have not yet been investigated. Efforts to find or fabricate soft bond concepts have been primarily directed at obtaining materials with the appropriate linear elastic moduli for use in specimen fabrication for concept verification testing. The obtainment of materials that also exhibited high bottoming strains was only a secondary consideration. Bond line sizing studies for a representative reentry vehicle indicated that if bond bottoming is detrimental, it is necessary to utilize soft bond concepts that have high bottoming strains in order to achieve thin bond lines. If bond line thicknesses have to be made large to avoid bottoming, it is possible that the soft bond concept may then not offer systems weight advantages over other hardening concepts. However, the magnitude of bond thickness at which use of the soft bond concept ceases to be advantageous is highly dependent upon the system and system geometry to which the concept is applied and this magnitude has not yet been determined for any representative entry system.

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## CHAPTER 4

### STRUCTURAL ADHESIVES DEVELOPMENT

#### 4.1 Purpose, Definition, and Scope

The purpose of this chapter is to summarize the present state of development of high-performance structural adhesives for use in the air frame, aerospace, and ordnance industries and in the construction of ships and military vehicles and to discuss specific problem areas and shortcomings in adhesive formulations now available.

A useful test of whether or not an adhesive type is included in the scope of this survey is its use in bonding metals and other nonporous high-modulus adherends such as fiber-reinforced composites and its long-term ability to transmit stresses within design limits under a wide variety of environmental conditions. It is probably not advisable to define "permanence" in terms of tensile shear strength or some other single arbitrary test value unrelated to stress-strain or crack propagation characteristics. Permanence of an adhesively bonded joint depends upon many factors in addition to the adhesive or the method of application. Among these other factors are the design of the joint, the method of surface preparation, the extremes of high or low temperatures encountered in service, stress level, the loading history, and exposure to adverse environments.

A small number of types of thermosetting resin adhesives, developed during the past 30 years, are able to provide useful bond strength levels over an extremely wide use-temperature range and, moreover, can survive many years of outdoor weathering, thermal cycling, and exposure to corrosive liquids and vapors. Although a few thermoplastic resin types might be used by themselves for some of these applications (generally at the lower temperature levels), the requirement that an adhesive joint be creep resistant -- able to resist plastic deformation under long-term loading and under a range of temperature and moisture conditions -- almost inevitably demands that the resin molecules be cross-linked during the process of forming and curing the bonded part.

#### 4.2 State of the Art

Structural adhesives are conveniently categorized by physical form in which they are used. The major difference is between adhesives that are used as solids and those that are used as liquids (or spreadable pastes) in the absence of volatile non-reactive solvents. Included are:

- a. Solid adhesives
  - Film adhesives (unsupported)
  - Tape adhesives (supported)
  - Solid powders or other melt-applied thermosets
  - Solvent-based adhesives and primers.
- b. "100% solids" paste and liquid adhesives
  - One-component, long shelf life
    - (1) Heat cured
    - (2) Frozen adhesives; room-temperature cured
    - (3) Cured by surface or anaerobic catalysis
  - Two-component; short pot life
    - (1) Room-temperature cured
    - (2) Heat cured

A recent book (Bolger 1973) gives a complete description of the chemical composition and methods for manufacturing, using, and curing each of the above types of adhesives. Relative performance data are also given.

Not all of the adhesives listed above and described by Bolger (1973) fall within the scope of the present study. This study excludes: sealants (silicons, assembly operations, for which very high bond strengths are not necessary, and for thread sealing; cyanoacrylates, anaerobic-cured acrylics, and most liquid epoxies and polyesters; epoxies and other resins used as binders for composites; and also inorganic or ceramic-base adhesives.

The specific resin system to be discussed herein will be limited to:

**a. Tape and film adhesives**

- Vinyl-phenolic and nitrile-phenolic
- Epoxy-phenolic
- Nylon-epoxy
- Nitrile (or other elastomer) modified epoxy
- Polyimide and other heterocyclic aromatic polymers

**b. Paste and liquid adhesives**

- One-component heat-cured epoxy
- Two-component room-temperature curing epoxy
- Amine-cured polyisocyanate

**4.2.1 Tape and Film Adhesives**

The distinguishing compositional feature of tape and film adhesives is their large proportion of high-molecular-weight polymer. While a typical "100% solids" paste or liquid adhesive must contain only low-molecular weight resins in order to flow and spread, tape and film adhesives frequently contain resins that have a molecular weight of 20,000 or more. Network polymers made from these long chains can be considerably tougher and more resilient and can provide more recoverable elongation than the short, highly-branched and random networks formed by curing the low-molecular-weight resins found in paste adhesives.

Figures 5 and 6 (see pages 66 and 67) illustrate this point by comparing typical tensile shear data reported for Al/Al lap shear tests (ASTM D-1002) by the manufacturers for a variety of adhesive types. The base of the tape and film types have higher peak values and broader useful temperature ranges than the best of the liquid adhesives types.

A newer approach to adhesive characterization in bonded joints involves testing with a high strain density ( $10^{-6}$  to  $10^{-8}$ ) extensometer. This promises to lend more definitive direction to adhesive formulation. Using microstrain testing techniques it has been shown that certain adhesives in bonded joints exhibit stress-strain curves with linear portions.

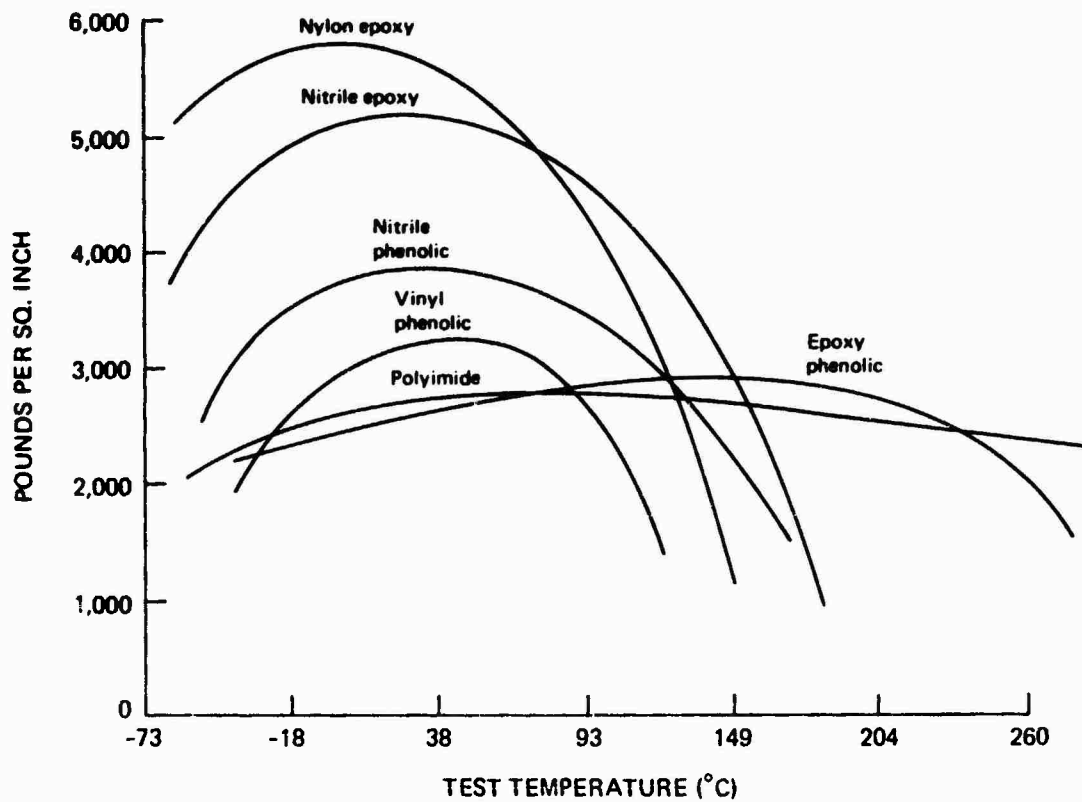


FIGURE 5 Typical tensile shear data for tape-, film-, and solvent-based adhesives (per ASTM Standard D-1002).

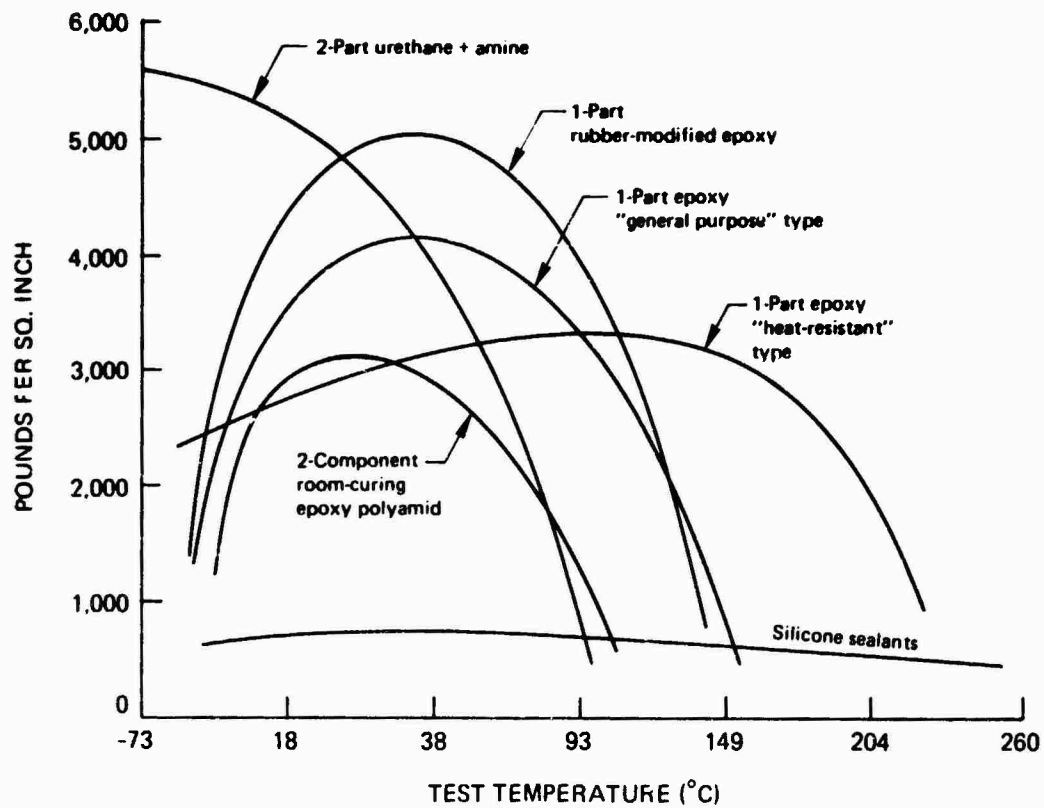


FIGURE 6 Typical tensile shear data for paste and liquid (100% solids) adhesives (per ASTM Standard D-1002).

Using this technique it has been shown that a nylon carrier may influence the linear portions of the stress-strain curves undesirably (Rutherford and Hughes 1968).

Microstrain techniques also may be used to observe beneficial effects of fillers on mechanical properties. At the same time electrical properties are altered. The dielectric constant becomes stress sensitive; thus, a capacitance extensometer that involves measurements through the bond is formed. This effect was observed as early as 1956, and filling adhesives to gain increased thermal and electrical conductivity has led to similar problems\* (Minford 1973, Norris et al. 1956).

Although peel strength is not usually design criterion, the manufacturer of bonded assemblies is extremely interested in achieving high peel strength. The designer recognizes the damping characteristics associated with a high peel strength system and the resultant improved impact and fatigue resistance. The manufacturing engineer prefers high peel strength because it is an easily measured process control property and reduces the potential for accidental damage during the assembly of the part. Consequently, good peel strength is sought from the adhesive formulator.

Tape and film adhesives have major handling and reliability advantages. They come ready to use, require no mixing or degassing, and eliminate possibilities for errors in adding catalyst. Tapes can be tested by vendor as well as by user. It is common practice for airframe manufacturers to run bond tests on small patches of material cut from every roll of adhesive tape received. Tape adhesives also facilitate a variety of lay-up techniques whereby large wing or tail structures can be assembled from skins, support spars, honeycombs, and edge members. These are interleaved with pre-cut sheets of tape, and then assembled, inspected, clamped, cured, and re-inspected to yield a virtually defect-free structure. The support mesh of tape adhesives also serves to control

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\* Recent applications of adhesive bonding in missiles has again revived this problem.

the bond line thickness avoiding adhesive-starved areas where curvature or external bonding pressure is highest.

On the other hand, these lay-up procedures are slow and costly. In addition, it is costly to buy an adhesive as a tape both because wastage of cut-away tape sections, and because the procedure of manufacturing a tape adds so much to the cost per unit volume of adhesive ultimately used. These factors favor use of film, paste, and liquid adhesives where design allowables permit.

Although hundreds of tape and film adhesives are now listed in manufacturer's catalogs, these are in fact composed of a relatively small number of combinations of the following three components:

- a. A high-molecular-weight "backbone" polymer, such as nylon or a nitrile rubber, that provides the elongation, toughness, and peel properties of the adhesive
- b. A low-molecular-weight cross-linking resin, usually either an epoxy or phenolic type.
- c. A curing agent for the cross-linking resin

Tape and film adhesives are named according to the identity of resin components a and b (e. g., nitrile-phenolic, nylon-epoxy, etc.) and, therefore, also are frequently referred to as "two-polymer" adhesives.

Whereas older adhesives, based on phenolic cross-linking resins, liberate volatiles and some require high bonding pressures to prevent void formation during cure, the newer adhesive types, based on 100% reactive epoxy resins do not evolve volatiles during cure. Bonding pressure depends, however, on factors other than volatile evolution. In addition to maintaining alignment and compensating for resin shrinkage during bonding, pressure also serves to improve flow and contact by the adhesive and it helps to remove air and volatiles by causing some of the adhesive to extrude out of the bond line in the molten condition. Hence, bonding pressure also depends on the compliance of the surfaces to be bonded and on the melt viscosity of the adhesive during cure.



#### 4.2.1.1 Vinyl-phenolic and Nitrile-phenolic Adhesives

The first successful structural adhesive was developed in the United Kingdom during World War II for assembling DeHavilland aircraft. It was named the Redux adhesive system by its inventors at the Aero Research Corp. Bonds were made by spreading a resol phenolic resin solution on the parts to be bonded, then sprinkling a powdered polyvinyl formal resin on to the surface, allowing the solvent to evaporate, assembling the joint, closing the bond, and curing with heat and pressure. Crude as this technique sounds by today's standards, bonds made with Redux adhesives provided very much higher strength and durability than had ever before been obtained in any synthetic resin metal-bonding adhesive. This was the starting point from which all such modern structural adhesive systems have evolved. The Redux system was the first to demonstrate the basic principle of toughening a thermosetting resin with a high-molecular-weight linear polymer.

Shortly thereafter, this two-polymer principle was used to blend Novolac-phenolic resins with a high-molecular-weight synthetic elastomer, plus other compounding ingredients, to produce the class of solvent-based liquid and film adhesives known as the nitrile-phenolics. Because of cost advantage, plus slightly higher service temperature ratings, the nitrile-phenolics, particularly in thin-film form, began to replace the vinyl-phenolics in airframe assembly, and later they found large volume automotive use in bonding brake shoes and clutch discs.

Phenolic-cured adhesives had, and continue to have, one major performance advantage -- i.e., bond durability -- that is still not matched by the newest epoxy-cured systems. Many authors (Bodner and Wegman 1969; Black and Blomquist 1962) over the years have documented the exceptional capability of the best vinyl-phenolic, nitrile-phenolic, and epoxy-phenolic adhesives to retain bond strength on aluminum or other metals after extended exposure to combinations of moisture, salt, stress, and impact.

Although the vinyl - and nitrile-phenolic adhesives continue to be used for non-aerospace bonding (e.g., brake shoes), they have largely been displaced for

aircraft assembly by the newer epoxy-elastomer adhesives. Three major application disadvantages of the phenolic systems are slow rate of cure, high cure temperature, and high pressure needed during cure to prevent void formation.

As the size and complexity of bonded assemblies increased, airframe manufacturers began to demand the lowest possible cure time, temperature, and pressure to minimize the required number and size of their autoclaves. In addition, although the performance properties of these systems could be varied by adjusting the ratio of phenolic resin to modifying polymer (e. g., lowering the phenolic content and giving up some hot strength and moisture resistance in order to gain greater peel strength and increased flexural properties), the total available "trade off envelope" did not yield the higher peel strengths demanded by designers and ultimately provided by the faster, lower pressure curing nylon-epoxy and nitrile-epoxy systems. (See Figure 8, page 80.)

#### 4.2.1.2 Epoxy Phenolics

One type of phenolic-based adhesive continues to retain a specialized, but important, position. Solid bisphenol-A based epoxy resins have about the same hydroxyl functionality as do adhesive grades of polyvinyl butyral or polyvinyl formal and undergo the same types of condensation reactions with phenolic resins. Use of the epoxy back-bone polymer as the polyol, however, resulted in a major improvement in thermal stability, albeit at the predicted decrease in flexibility, elongation, and peel values (Black and Blomquist, 1952)

Despite the fact that it is now over 20 years since the first Forest Products Laboratory formulations were published, and despite the enormous effort that has gone into the development of new polymeric systems designed for use at elevated temperatures, epoxy-phenolics are still considered to be the best adhesives available for up to several hundred hours service in the 175 to 260°C temperature range. (Chapter 3 describes the use of these epoxy-phenolic adhesives in the high temperature areas of manned spacecraft.)

#### 4.2.1.3 Nylon-epoxies

When nylon-epoxy adhesives were developed during the early 1960s, they

appeared to herald a new age in adhesives. Where adhesives technologists had tried for two decades to provide more than about 50 lb/in. peel strength, these nylon-epoxy adhesives provide a major jump in toughness--yielding climbing drum peel strengths above 100 lb/in., in lap-joint tensile shear strengths upwards of 5000 psi, and exceptional fatigue and impact properties.

Although these exceptional bond values have won for the nylon-epoxies some important applications, notably in the lamination and assembly of metal helicopter rotor blades, this class of adhesive has one serious drawback which limits its present aerospace use. Nylon-epoxy films not only have the unfortunate tendency to absorb water before cure but, also the more troublesome tendency to lose bond strength rapidly after cure upon exposure to water or moist air (Minford 1943; Norris et al., 1956; Sharpe, 1966). During the past 10 years, many R & D programs have been aimed at developing primers or other methods for reducing the moisture sensitivity of the nylon-epoxies. Although some of these techniques undoubtedly prolong service life, as evidenced by the good service life of helicopter rotor blades, it does not now appear possible to achieve the desired bond durability using adhesives containing a high proportion of nylon as can be done with nitrile-rubber or acetal-epoxy film adhesives.

#### 4.2.1.4 Elastomer-Epoxy

The modern trend in aircraft adhesives is toward epoxy resins toughened with an elastomer (most frequently a nitrile rubber). The epoxy is cured with catalysts based on dicyandiamide which permits cure at low pressure in short time and at a low temperature. Early phenolic-based tape adhesives required cure above 150°C, but the use of adhesives to assemble progressively larger wing, tail, and fuselage sections has placed a premium on lower cure temperatures in the 80 to 120°C range (permitting the use of lower steam pressures and thinner-walled autoclaves), and on shorter cure cycles, permitting more units to be assembled per autoclave per day.

The improvement in tensile shear and peel strength obtained by adding nitrile rubbers compares favorably to the improvement obtained by adding nylon to

rigid epoxy adhesives, although the maximum bond values are still considerably below those attainable with the nylon-epoxies at room temperature (see Figure 5). A major advantage of the nitrile-epoxy adhesives, however, is that bond durability with the high-peel elastomer-epoxies is reasonably good as measured by most long-term moisture exposure tests.

#### 4.2.1.5 Adhesives for High-Temperature Use.

The decade from about 1956 to 1966 witnessed a nation-wide effort to develop a new generation of polymers intended for use at temperatures above 260°C. Much of this work, involving fluorocarbon or silicone elastomers, was an extension of previous technology, but this period also marked the peak of activity with many entirely new types of heterocyclic aromatic polymers, including the polyimide (PI), polybenzimidazole (PBI), polybenzotriazole, and other condensed ring linear polymers. Some of these retain useful strength levels after extended service at 315°C. in air and others after exposures of short duration at up to 540°C. The data of Figure 7 (page 74) refer to service temperatures up to one hour duration in air (Figure 7 - courtesy of H. Schwartz, U. S. Air Force)

Table I compares longer-term bond strengths for a typical PI, a PBI, and an epoxy-phenolic adhesive. It shows that the PI and PBI adhesives produce higher bond strength above 260°C in air than a typical epoxy-phenolic adhesive, although the latter gives better strength retention after exposure to water or other polar liquids at lower temperatures.

One disadvantage of these aromatic polymers is the problem of eliminating volatiles during cure. In part, this is because the only solvents for the pre-polymers are high boiling, polar solvents such as dimethyl formamide, dimethyl acetamide, cresol, N-methyl pyrrolidone-2. In addition, cure consists of converting the thermoplastic pre-polymer to the insoluble virtually impermeable final polymer by internal ring closure, a process that requires driving off up to 15 percent by weight of water, alcohols, or other condensation product.

Thus, to obtain a void-free bond, these adhesives require a long and careful series of cure steps at temperatures of from 315 to 370°C accompanied by

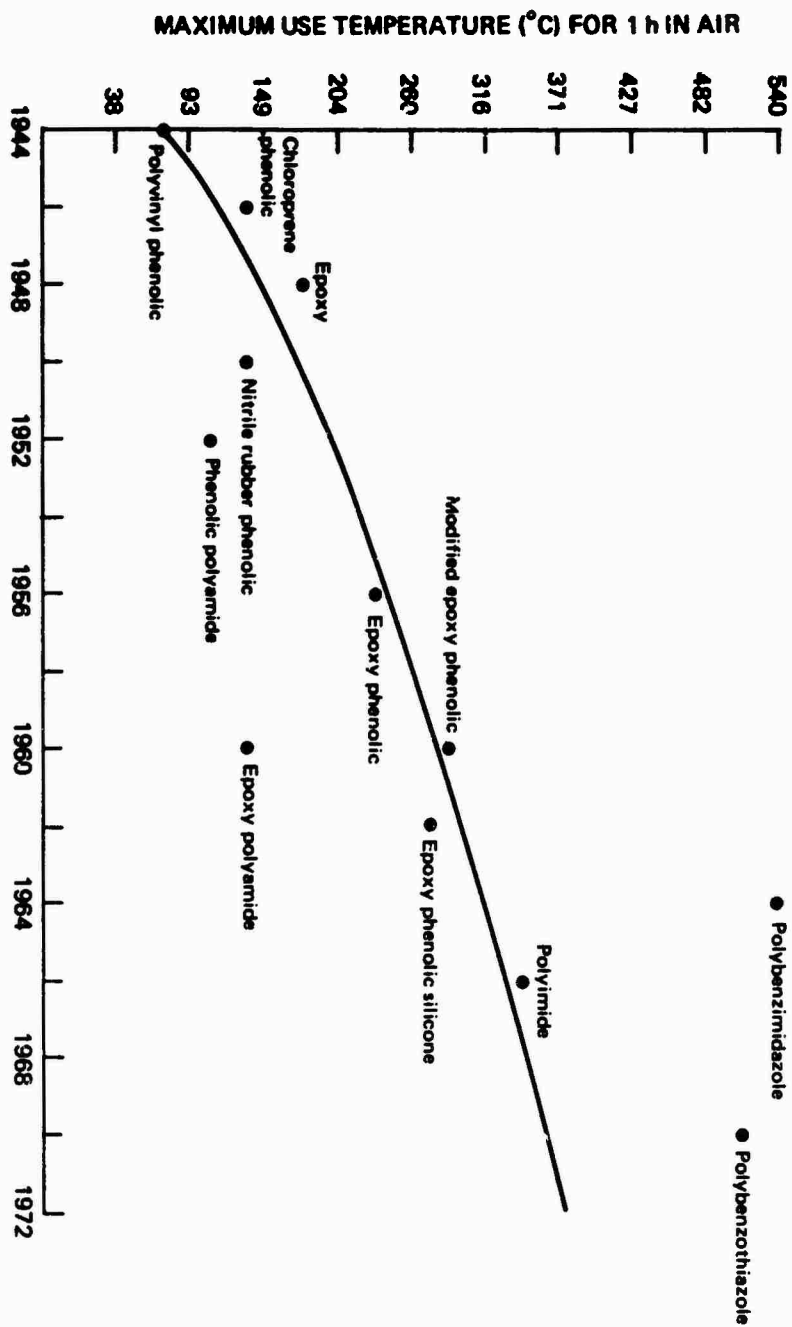


FIGURE 7 Sequence of development of heat-resistant adhesives.  
(Courtesy of H. Schwartz, USAF)

Table I Bond Strengths of High-Temperature Adhesives (Ikeda 1964; Twiss 1966)

Tensile Shear Strength	PI-1101	PBI	Epoxy Phenolic
Initial; at 25°C (3)	2800	4000	4000
at 288°C after 1 hr	1600	3500	2100
" 10 hr	1900	2500	0
" 1000 hr	1400	0	0
at 371°C after 1 hr	1300	2000	900
" 10 hr	1100	2000	0
" 60 hr	1100	0	0
at 25°C after:			
30 days, tap water	2100	1900	2600
30 days, 43°C, 100% R. H.	1900	1900	2900
30 days, 5% salt spray	2000	1900	3200
7 days, isopropyl alcohol	2600	3300	4000

NOTE: PI and PBI adhesives compounded with arsenic stabilizer and aluminum powder. Epoxy-phenolic compounded from Epon 1001, resol phenolic and aluminum powder. All on heat cleaned 112-E glass mesh carrier, applied to phosphate etched 304 stainless steel. The PI-1101 had a bond thickness of 3 to 6 mils and a cure cycle of 2 hr at 302°C and 200 psi; the PBI had a bond thickness of 3 to 5 mils and a cure cycle of 1 hr at 316°C and 200 psi; and the epoxy-phenolic had a bond thickness of 8 to 10 mils and a cure cycle of 1 hr at 177°C and 50 psi.

intermittent application and release of high clamping pressures. These processing problems, together with their high cost, relative brittleness, and low peel values presently limit the use of these adhesives.

Of the many aromatic polymers once considered as candidates for the high-temperature-resistant adhesives of the future, the polyimides are now considered the best choice for long-term service at 260 to 370°C. The polyimides have advanced largely because of the extensive commercial development work done by E. I. DuPont de Nemours and Co., the Monsanto Co., and others. This work was aimed at developing non-military, non-adhesive markets for the polyimides, e.g., as high-temperature wire enamels and dielectric materials.

#### 4.2.2 Paste and Liquid Adhesives

While there exist many possible types of curing agent for epoxy resins, two types are most frequently used in high-performance adhesives. Aliphatic amines, generally modified by pre-reaction with aliphatic acids to form the so-called polyamid curing agents, are used for two-part systems that cure at or slightly above room temperature. The second important curing agent is dicyandiamide, normally used with an accelerator, for one-part heat-cured epoxies. As has been noted, dicyandiamide is also the major curing agent in the nylon-epoxy and nitrile-epoxy tape and film systems.

##### 4.2.2.1 One-Part Heat-Cured Epoxies

The best adhesives of this type can be regarded as low-molecular-weight analogs of the nitrile-epoxy tapes. They are based on a liquid epoxy resin, cured with dicyandiamide (plus promoters to reduce the cure temperature into the 95 to 135°C range). They contain a minor quantity of a liquid nitrile rubber, plus colloidal thickening agents to provide "non-sag", gap-filling properties. Such pastes give tensile shear and peel strengths that approach those of their tape and film analogs (see Figure 6). For both the solid and the liquid versions, however, best mechanical properties of the cured joint are obtained at cure temperatures about 150°C and without accelerators to speed the dicyandiamide initiation temperature. Peel and tensile properties begin to fall off, ultimately reaching unacceptable

levels at cure temperatures below about 105°C. A second limitation for these systems is that dicyandiamide-epoxy formulations have a high exotherm; this results in charring and vaporization except when the adhesive is cured in thin films.

#### 4.2.2.2 Two-Part Room Temperature-Cured Epoxies

Of all the useful groups that can add to an oxirane ring, only aliphatic amines and mercaptans do so effectively at room temperature. The best adhesives, which have evolved from this limited choice of starting materials, are the amine-terminated polyamid-cured epoxies (akin to the type sold in hardware stores for home repair use). While the tensile properties of optimized adhesive systems of this type are useful at room temperature, these adhesives have a very narrow service temperature range, becoming brittle below and soft just above room temperature (see Figure 6). Peel strengths are low at all temperatures. Finally, many authors (Rutherford and Hughes 1968; Twiss 1966) have shown that these systems are prone to fail at low stress levels in the presence of moisture.

#### 4.2.2.3 Amine-Cured Diisocyanate-based Adhesives

Diisocyanate-based "polyurethane" adhesives are widely used for bonding elastomers, fabrics, fibers, and thermoplastics. Polyurethane adhesives were, in fact, first developed in Germany during World War II specifically for bonding rubber to metal tank treads. They continue to represent an excellent choice for bonding metal to plastics or elastomeric adherends. But the tensile modulus of most diisocyanate-based adhesives, although high enough to yield bond strengths that can "tear rubber" during fracture, is too low to provide the tensile shear strength and level of creep resistance required in most metal-to-metal bonding applications in aerospace. Adhesives made from diisocyanates also have the disadvantage of poorer chemical and thermal stability than most epoxy adhesives; they lose bond strength at temperatures above about 80 to 100°C. Many authors (Smith and Susman 1963; Twiss 1966) pointed out that the best of the polyurethane adhesives are superior in performance to virtually any other adhesive type at cryogenic temperatures. These adhesives maintain their shear



strength and toughness at temperatures far below those that cause serious embrittlement of other types of adhesives designed for use at ambient temperatures and above.

The polyurethanes shown in Figure 6 might more properly be called polyurea adhesives since these are hydrolytically stable\* heat-cured two-component systems made by reacting an isocyanate-terminated prepolymer with an aromatic diamine to form a substituted urea. Optimum mixing ratios usually provide for about a 10 percent molar excess of diisocyanate. The very rapid diisocyanate-diamine reaction first produces a long chain linear polymer, after which cross-linking occurs by reaction between the excess-NCO groups and-NH groups along the chain. The toughness and high elongation properties of these adhesives derive from the incorporation of long-chain, linear polyether segments in the prepolymers.

The low cohesive strength of a polymer made from long-chain aliphatic polyethers is balanced by the regions of very intensive hydrogen bonding at the urea linkages. This combination of long, flexible, weakly bonded polymer chain segments alternated with regions of strong secondary force attractions accounts not only for the balance of low-temperature flexibility and room-temperature tensile strength but also for the rapid falloff in adhesive modulus and tensile properties on heating. Moisture resistance is just moderate and primers are almost invariably required for maximum durability of metal-to-metal bonds.

The very short pot life of these two-part systems, coupled with the need to melt the solid amine curing agents just before mixing these with the resin requires either that elaborate heating, mixing, metering, and dispensing equipment, be used for 100 percent solids adhesives or that one or both components be cut back with a volatile solvent. While these adhesives will cure at room temperature, a heat cure, typically one hour at 100°C, is needed to develop the bond strengths shown in Figure 6.

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\* See Chapter 3.

### **4.3 Identification of Problem Areas and Development Objectives**

#### **4.3.1 Lower Costs**

Most presently used adhesive systems for aerospace structural bonding applications are supplied in the form of a thin film that is applied to the area to be bonded by a process of cutting out suitably shaped pieces to fit the part. This is an expensive hand lay-up procedure and also results in many small pieces that must be discarded; hence, the adhesive scrap rate is high.

#### **4.3.2 Ability to Bond to Wider Range of Adherend Types**

Traditionally, epoxy and phenolic-based structural adhesives have been developed and optimized for use on FPL-etched aluminum. These adhesive systems may have less strength or durability on other metals or with non-metallic adherends. Continued R&D effort is needed on new adhesive systems for use on titanium, stainless steel, magnesium, beryllium and fiber-reinforced composites. By adhesive "system" is meant that the adhesive composition itself must be considered as well as the method of preparing the surface, the possible use of primers, and the method of application and cure of the adhesive.

#### **4.3.3 Improved Toughness, Heat Stability, and Other Performance Properties**

Improved "toughness" properties such as crack resistance and fatigue strength, are continually demanded, and needed, by airframe designers. But, at the same time designers also require improvements in such "durability" parameters as strength at elevated temperatures (see Figure 7), longer service life times at higher operating temperatures, and improved resistance to water, humid air, salt, hydraulic fluids, and other corrosive media. Gains in any of the toughness parameters can be regarded as a true advance in the state of the art only when achieved without major sacrifice in one or more of the durability parameters (Figure 8). Generally speaking, improving any of the toughness properties requires synthetic or formulation changes (such as reducing the covalent cross-link mass density, increasing chain length and chain segment mobility, and other morphological factors). These tend to reduce one or more of the durability parameters. Hot strength and water and chemical resistance

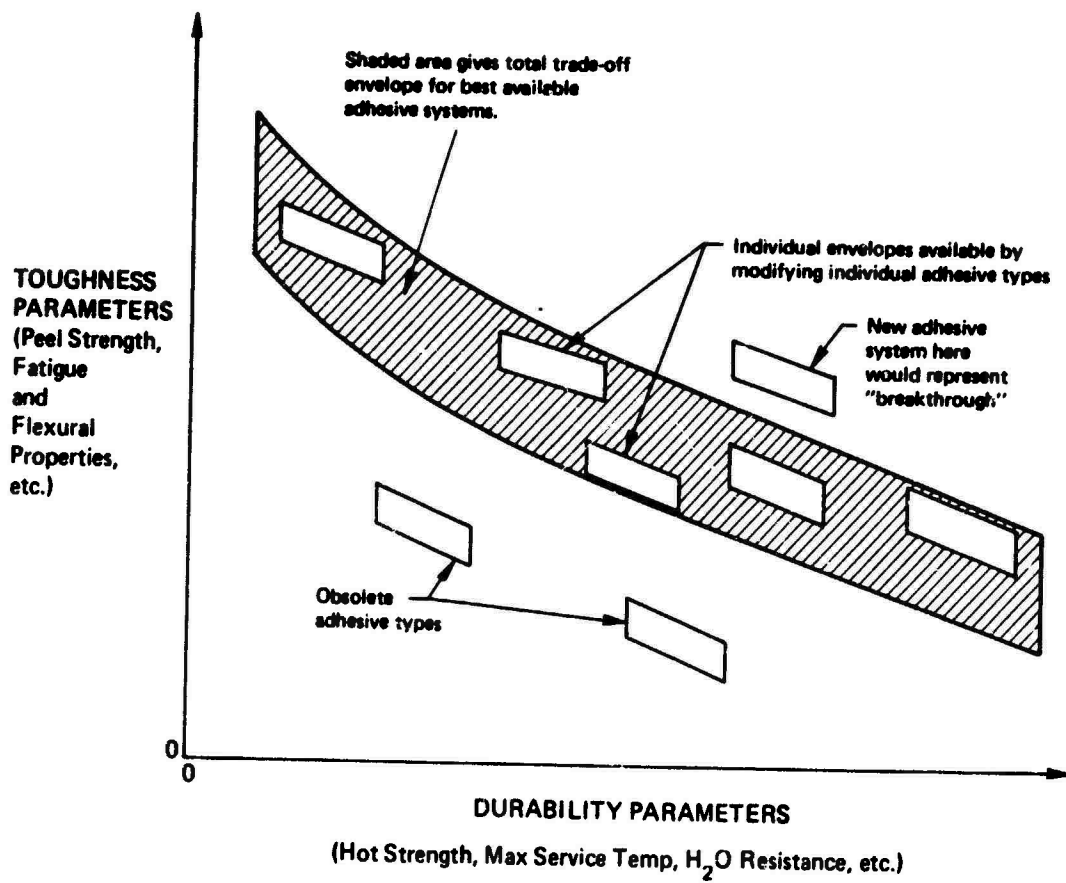


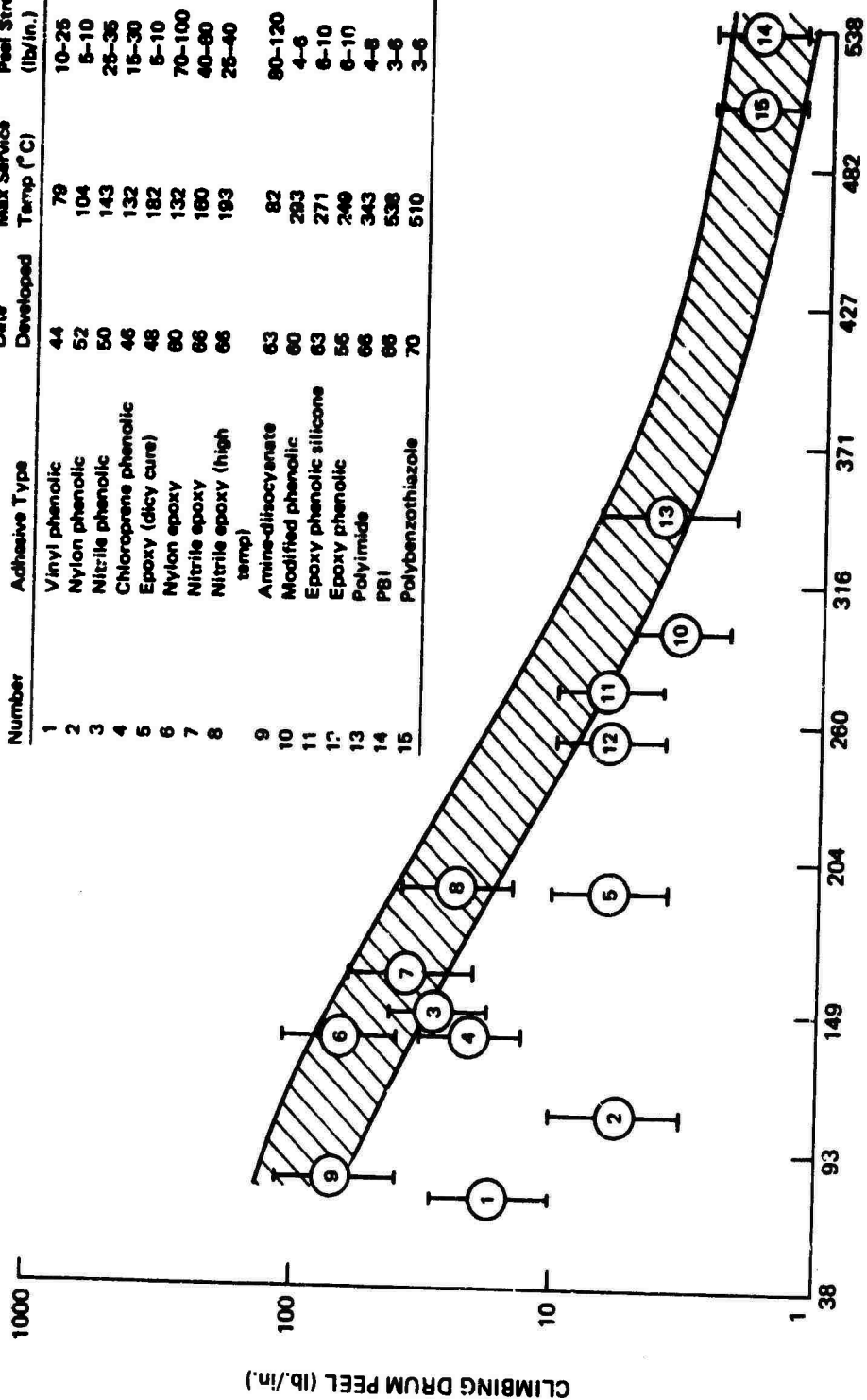
FIGURE 8 Best available trade-off between conflicting toughness and durability requirements, based on state of the art.

are improved by going to rigid, tightly cross-linked networks, of primarily aromatic character, or by using high-filler loadings or other factors that reduce elongation and toughness. Any competent formulator, operating with the best available polymeric starting materials plus the best curing and compounding methods, can generally move anywhere within a trade-off envelope as in Figure 8 which represents the best state of the art at a given time. But it requires a real breakthrough to move up and to the right, and this may require basic advances in polymer science and engineering. To illustrate this point, Figure 9 plots one toughness factor (peel strength) against one durability factor (maximum service temperatures taken from Figure 7). The best present tape and film adhesives are at the top edge of the envelope, with obsolete systems down and to the left. Real "progress" over the past 30 years has not come from a methodical optimization of combinations of existing materials, but rather by exploiting a small number of real breakthroughs. These breakthroughs have been:

- a. Initial recognition of the two-polymer principle of "alloying" a rigid thermoset with a high molecular weight linear polymer
- b. Development of bisphenol A-based epoxy resins and, starting about 1950, their increasing use in structural adhesives
- c. The synthesis of poly-aromatic polymers permitting service temperatures of adhesives above those previously known for epoxy, or phenolic-based systems.
- d. The development of special polymers--particularly those nylon and nitrile polymers whose solubility, crystallinity, functionality and other factors made these specifically compatible with epoxy resins in adhesives.
- e. The evolution of the polyphase principle which recognized that the way to move out of the trade-off area imposed by the morphology of a homogeneous polymer was to achieve a multiphase resin system wherein one or more dispersed (e.g., nylon-, or nitrile-rubber elastomer) phases could serve to toughen, e.g., serve as crack stoppers, within a more rigid, continuous, epoxy-rich resin phase.

Key

Number	Adhesive Type	Date Developed	Max Service Temp (°C)	Climbing Drum Peel Strength (lb/in.)
1	Vinyl phenolic	44	79	10-25
2	Nylon phenolic	52	104	5-10
3	Nitrile phenolic	50	143	25-35
4	Chloroprene phenolic	46	132	15-30
5	Epoxy (dicy cure)	48	182	5-10
6	Nylon epoxy	60	132	70-100
7	Nitrile epoxy	66	180	40-60
8	Nitrile epoxy (high temp)	66	193	25-40
9	Amine-diisocyanate	63	82	80-120
10	Modified phenolic	60	293	4-6
11	Epoxy phenolic silicone	63	271	6-10
12	Epoxy phenolic	56	249	6-10
13	Polyimide	66	343	4-8
14	PBI	66	538	3-6
15	Polybenzothiazole	70	510	3-6



MAX SERVICE TEMPERATURE (°C) FOR 1 HR. IN AIR

FIGURE 9 Peel strength vs. maximum use temperature, tape and film adhesives.

#### 4.3.4 Lower Cure Temperatures and Improved Cure Techniques

New epoxy-resin catalyst systems, possibly not based on dicyandiamide, that can cure more rapidly and/or that can cure below 90 to 105°C are needed to give properties as good as those obtained with dicyandiamide systems at higher temperatures. Also needed are epoxy-catalyst combinations that cure at room temperature and provide better strength, toughness, and durability properties than the epoxy-polyamides shown in Figure 6.

Meanwhile, new cure techniques that represent an improvement over the traditional ovens or steam autoclaves are needed. Why must it be necessary to spend hours heating up an entire air-frame assembly in order to heat just a few pounds of adhesive? Thus, more effort must be aimed at developing new high-speed, high-heat-input cure techniques, particularly those where the heat can be localized in the immediate area of the adhesive bond. These techniques may include induction heating, dielectric heating, focused infra-red resistance heating and ionizing radiation cure techniques.

#### 4.4 Recommendations

One or more development programs aimed at providing the above technical advances should be initiated by U.S. adhesive manufacturers who have demonstrated prior ability to develop advanced aerospace structural adhesive systems. Because of the present depressed financial condition of the aerospace adhesives industry, it is improbable that such programs would be initiated and completed successfully without government action and financial support. Therefore, the appropriate contracting agencies should implement these objectives by soliciting proposals and, thereafter, supporting and monitoring these adhesive development programs. One suggested technique, which could serve as a model for the present case, has recently been used by the Naval Air Systems Command in N00019-73-B-0169. This solicitation requests domestic firms that have at least five years of proven and relevant experience in formulating epoxy potting compounds to bid on developing a new compound having certain electrical and physical properties not available in present generation epoxies or urethanes.

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## CHAPTER 5

### INTERFACIAL ASPECTS OF STRUCTURAL ADHESIVE BONDING

#### 5.1 Introduction.

The strength of a bonded joint is often determined by the physical and chemical properties of the material in the neighborhood of the adhesive/adherend interface. An obvious example is the presence of a mold release substance on the adherend. Also, the interfacial region is usually sensitive to water and is therefore sometimes the locus of moisture-induced adhesive bond failure. Finally, the stress distribution in certain joint designs is such as to focus the failure into the interfacial region for purely mechanical reasons.

The properties of the adhesive/adherend interface depend not only on the surface characteristics of the adhesive and the adherend, but also on the surface phenomena that occur when the two are brought together. At present it is not possible to predict the properties of the bond interface from the known surface properties of the adhesive and the adherend. The best that can be done is to point to those surface aspects that are judged to be important. Cataloging these surface phenomena affords an opportunity to point out their importance to both the supplier and the user of adhesives.

The major structural materials in aerospace construction are metals and advanced composites. The emphasis in this chapter will be on metal adherends because they are the principal structural material and because most of the information presently available concerns metal-resin adhesion. Some of this information is also applicable to the bonding of composites. As for the adhesive, this chapter will deal only with those based on the synthetic polymers. Finally, it would be impossible and inappropriate to discuss the various surface aspects in full detail. Consequently, in presenting the state-of-the-art review in Sections 5.2-5.6, the reader will be referred to texts, review articles, and key research papers for additional information.



## 5.2 Adherend Surface

### 5.2.1 Chemical Composition

The surface characteristics of a metal are largely determined by its oxide film. The pertinent property of the oxide is its crystal structure (or lack of it), including its degree of hydration. There is an abundance of information on the growth and chemical structure of metal oxide films in general (Kubaschewski and Hopkins 1962; Evans 1960) and specifically for metals of interest to aerospace such as aluminum (Van Horn 1967), titanium (Jaffee and Promisel 1970), and magnesium (Raynor 1959). On the metal surface, in addition to the oxide, there will be water (both adsorbed and chemically bound) and various contaminants including inorganic salts and organic materials. If the inorganic contamination includes hygroscopic ions, these can lead to the apparent adsorption of many monolayers of water even if there are only trace amounts ( $10^{-7}$  gm/cm<sup>2</sup>) of these ions (Bowden and Throssel 1951). This "adsorbed" water can interfere with the spreading of the adhesive liquid (Shofrin and Zisman 1967). Also, it can act as a weak boundary layer. However, the most serious aspect of any hygroscopic contamination is that the adsorbed liquid collects as microdroplets (Bowden and Throssell 1951) of solution that can be strongly alkaline and capable of chemically attacking many metals.

In technical practice, adherends are frequently treated with a primer or adhesion promoter to the extent that a film much thicker than a monomolecular layer is left on the surface. Penetration of these films by the adhesive can produce an interfacial region vastly different from the bulk adhesive. Indeed, the effectiveness of these surface treatments may depend on their in-depth interaction with the adhesive (Bascom 1972).

Adsorbed organic material, which is hard to control in industrial atmospheres, can adversely affect the wettability of the adherend (Zisman 1965) and, if present as more than a single molecular layer, it may act as a weak boundary.

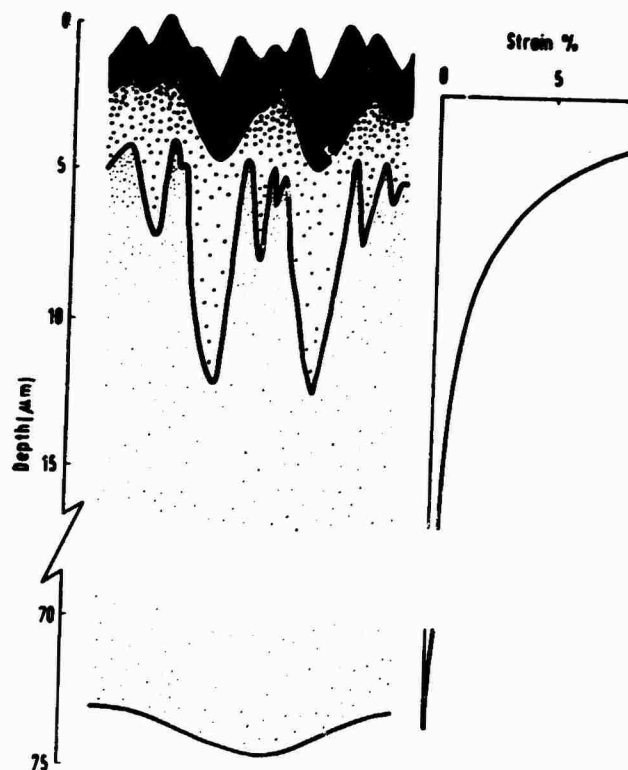
### 5.2.2 Mechanical Properties of the Surface Layer

Prior to bonding, the adherend is subjected to a number of mechanical

or chemical treatments that dramatically influence the properties of the surface. Machining a metal, for instance, introduces considerable surface strain as indicated in Figure 10 taken from the work of Samuels (Samuels 1971). Note the strain in the first few microns, and the considerable depth into the metal before this strain goes to zero. The situation is even worse for polished or burnished surfaces (Samuels 1971). Indeed, any cutting, working or rolling of the metal invariably leaves the surface in some state of strain. This region of strain may be cohesively weak and cause poor bond strength. Even more important, the additional strain energy in the first few microns of metal surface adds to its susceptibility to corrosive attack by moisture (v. stress corrosion, 5.4.4) and so contributes to moisture-induced bond failure.

### 5.2.3 Chemical Treatment of the Adherend Surface

Usually the as-received metal is given a sequence of treatments beginning with washes to remove gross contamination, followed by one or more chemical etches, and finally a water rinse. These washes and etches remove organic contamination, loose oxide, and probably some of the strained surface layer. However, experience has shown that these empirically established cleaning procedures must be followed rigidly. Seemingly inconsequential changes in procedure often result in weak bonds, or bonds that are unusually susceptible to moisture. For example, it has been reported that in using the acid-chromate etch on aluminum, the final rinse must be made with tap water rather than deionized water because the latter leaves a thick, weak hydrous aluminum oxide (bayerite) on the surface whereas the tap water leaves a thin, cohesively strong monohydrate (Wegman 1964). Another example is the recent work on titanium adherends, in which it was shown that a phosphate-fluoride treatment is better than an alkaline etch, because the phosphate leaves an anatase-type oxide that is less moisture sensitive than the rutile-form oxide left by alkali. Both anatase and rutile are tetragonal, polymorphic forms of  $TiO_2$ , but rutile is more thermodynamically stable so that the anatase oxide produced by the phosphate etch eventually reverts to rutile with an accompanying loss in bond strength (Hamilton 1942).



**FIGURE 10** Profile of the strain distribution in the surface of a machined metal (Samuels 1971). Reproduced from METALLOGRAPHIC POLISHING BY MECHANICAL MEANS by L. E. Samuels (Pitman) with permission of the publisher.

In addition to surface cleaning and etching, the metal may receive further treatment to convert the surface to a corrosion resistant, non-reactive form. Examples of these conversion coatings are phosphated steel and anodized aluminum (Burns 1967). Bonding to these conversion coatings can present difficulties (McIntyre 1972), and some of the variables involved have been discussed in a recent symposium (Riel 1971).

The veneering or cladding of an alloy with a more anodic metal is one of the oldest methods of corrosion protection. For example, some aluminum alloys are clad with pure aluminum (or a more anodic aluminum alloy) so that the resulting composite has the mechanical properties of the alloy but is anodically protected by the cladding. However, adhesive bonds to a clad surface can prove to be more susceptible to moisture than the bonds to the unclad metal (Weiss and Cheever 1968). Discussion of this important point is deferred to a later section (5.4.4).

#### 5.2.4 Surface Roughness

In considering the roughness of a surface the distinction must be made between a topography that is essentially a network of open channels (e.g., machining scratches) and one that is a matrix of capillaries (e.g., certain conversion coatings). Flow of the adhesive into open channels is quite different from flow into a porous matrix (Mark 1967).

Other factors being equal, the topography of the adherend surface will influence the process of making a bond and the final bond strength. In the first instance, the surface rugosity will influence the flow of the adhesive perhaps to the point of preventing complete air displacement. However, even if the interface is void free, stresses may develop in the resin at surface asperities. These will be discussed further when considering bond preparation and interfacial stresses.

#### 5.2.5 Surface Analysis

Recent developments in surface science have made available very sensitive methods of surface analysis and, when combined with the more classical methods of surface examination, make it possible to fully characterize an adherend

surface. Many of the surface analysis techniques are based on radiation or particle scattering and can be fitted into a grid (Figure 11) according to the type of incident and scattered radiation or particle. This grid accommodates as old a technique as light microscopy and as novel a technique as ion scattering spectroscopy. In Table II, the analytical methods indicated on the grid and other techniques are listed according to the type of information generated. Clearly, a solid surface can be fully characterized--from its gross roughness down to its elemental surface composition. Table II and Figure 11 are not intended to be totally inclusive; in fact new developments in the lower right hand corner of the grid are coming too fast for any listing to be fully current. The reader is referred to the various references for details concerning any of these surface analysis techniques.

Contact angle measurements to assess wettability have had special significance in adhesion science for three reasons:

- The flow of the adhesive liquid onto the adherend surface is a wetting-spreading phenomena
- There is a fundamental relation between the contact angle and the thermodynamic work of adhesion,  $W_A$ ,

$$W_A = \gamma_{LV} (1 - \cos \theta)$$

where  $\gamma_{LV}$  is the surface tension of the liquid adhesive and  $\theta$  is the contact angle the liquid makes with the solid (measured through the liquid)

- Wettability measurements can give direct information about the molecular structure of organic (Zisman 1964) and inorganic (Zisman 1965) surfaces.

The interrelation between contact angles and the wetting-spreading behavior of an adhesive is discussed below (5.3.1). As far as the work of adhesion is concerned, it must be kept in mind that it is a small factor in determining bond strength compared to the inelastic work of deformation that must be done to break a joint. However, if  $W_A$  is a multiplication factor rather than a small additive

REFLECTED BEAM		INCIDENT BEAM					
		INFRARED	VISIBLE	ULTRAVIOLET	X-RAY	ELECTRONS	IONS
INFRARED		REFLECTION SPECTROSCOPY (MIRS)	RAMAN SPECTROSCOPY				
VISIBLE			ELLIPSOMETRY "LIGHT" MICROSCOPY REFLECTION SPECTROSCOPY				
ULTRAVIOLET				ELLIPSOMETRY REFLECTION SPECTROSCOPY			
X-RAY					X-RAY DIFFRACTION X-RAY MICROSCOPY	MICROPROBE APPEARANCE POTENTIAL SPECTROSCOPY	
ELECTRONS			PHOTOMISSION SPECTROSCOPY	ESCA	PHOTOELECTRON SPECTROSCOPY ESCA AUGER SPECTROSCOPY	LEED, RHEED ELECTRON MICROSCOPY AUGER SPECTROSCOPY	
IONS							ION SCATTERING SPECTROSCOPY ION-PROBE MASS SPECTROMETRY

FIGURE 11 Methods of surface analysis based on the examination of reflected radiation and/or particles. Abbreviations: MIRS, multiple interference reflection spectroscopy; LEED, low energy electron diffraction; RHEED, reflected high energy electron diffraction; ESCA, electron spectroscopy for chemical analysis.

TABLE II

## Methods Used for the Study of Solid Surfaces

## Macrostructure

microscopy (a, b, c)  
surface topography (d)  
friction measurements (e)  
ellipsometry (f)

## Molecular Composition and Structure

multiple interference reflection spectroscopy (g)  
Raman spectroscopy (h)  
ellipsometry (f)  
contact angle measurements (i)  
surface potential measurements (j)

## Crystal Structure

x-ray diffraction (k)  
low energy electron diffraction, LEED (l)  
reflected high energy electron diffraction, RHEED (m)

## Elemental Composition

photoemission spectroscopy (n)  
photoelectron spectroscopy  
    ESCA (o)  
    Auger (p)  
ion scattering spectroscopy  
    low energy (q)  
    high energy (r)  
ion-probe mass spectrometry (s)  
microprobe (t)  
appearance potential spectroscopy (u)

Reference: for Figure 11 and Table II

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term (Zisman 1964), its importance in bond strength would not be inconsequential.

The use of contact angle measurements as a means of characterizing organic surface films or polymer surfaces has become extensive among students of surface chemistry and the science of adhesion (Towkes 1967; Good and Elbing 1971; Zisman 1964). However, the indiscriminate use of contact angles as a means of determining surface molecular structure can be very misleading and should not be routinely applied to adherend surfaces without supplementary techniques.

The scanning electron microscope (SEM) has added a new dimension to microscopy in its great depth of focus at high magnifications ( $>1000\times$ ). However, it should be noted that at high magnifications it is very easy to "miss the forest." Indeed, SEM at low magnification and the ordinary light microscope (or its interferometry or fluorescence modifications) will give as much and often more information than can be obtained at high magnification with the scanning or transmission electron microscopes.

A final comment about the various techniques indicated in Figure 11: They can give detailed information about the composition, structure, and chemical bonding of surface molecules and atoms, but in the majority of cases the incident beam must penetrate the surface in order for the scattered beam to communicate any information. Consequently, the analysis is not necessarily that of the immediate surface but may include material hundreds or thousands of angstroms into the substrate. For example, the depth of penetration in infrared reflection spectroscopy or in microprobe analysis can be as much as  $0.5\text{ }\mu\text{m}$ , whereas the effective depth of penetration in ESCA and Auger Spectroscopy\* is only about 10 to 20 Å. The detection depth is so shallow in the latter cases because only the electrons from the surface atoms are able to escape into the detector even though the incident beam excites secondary electron emission hundreds or thousands of angstroms into the material. The depth of detection is also limited to the surface atoms in ion-scattering spectroscopy.

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\* Also known as autoionization.

### 5.3 The Adhesive

#### 5.3.1 Wetting and Spreading

Turning now to the surface behavior of the adhesive resin, the general statement is frequently made that the adhesive must "wet" the adherend surface. What is meant is that in bringing the adhesive and adherend together no air can be trapped at the interface. Ideally, three criteria must be met:

- a. The resin liquid should spread spontaneously i.e., the liquid surface tension is less than the critical surface tension of the solid (Zisman 1964)
- b. Some time during the bonding process the resin viscosity should be no more than a few poises
- c. The rate and manner at which the adhesive and adherend are brought together give the resin time to displace the air

The spreading criterion, a, is usually met for the case of a liquid organic polymer by a dry, metal oxide surface free of organic contamination (Zisman 1964). Note, however, that there is an important difference between the liquid exhibiting a very small but finite contact angle and a true zero contact angle condition. In the latter case, surface tension gradients can exist at the spreading front (due to thermal or concentration gradients) which can greatly assist or hinder spreading depending upon their direction (Bascom et al. 1964). When the contact angle is finite, albeit small, there is less opportunity for any frontal gradient. Another factor is that so long as the contact angle is less than 90°, liquid will be drawn by capillarity into surface scratches (Cottingham et al. 1964) and, given sufficient time, a nonspreading adhesive can wet a rough adherend. However, if the surface roughness is a microporosity (as opposed to open channel scratches), complete air displacement is difficult to achieve even under conditions of a zero contact angle (Zisman 1965).

The ideal spreading criterion, b, that the adhesive have a viscosity of a few poises, is seldom met in practice. Consequently, if the adhesive liquid is forced rapidly across the adherend surface during the bonding process, the

liquid near the surface cannot keep up with the advancing front so that an apparent dynamic contact angle develops. For most adhesives with viscosities from 10 to 1000 poise, the dynamic angle is best described by the Fritz equation (Fritz 1965; Schwartz and Tegada 1972):

$$\tan \theta_d = 3.4 \frac{\eta v}{\gamma_{LV}}$$

in which  $\eta$  is the viscosity,  $v$  is the spreading velocity, and  $\gamma_{LV}$  the liquid surface tension, all in cgs units. Clearly, the dynamic angle approaches  $90^\circ$  for a moderately viscous liquid ( $\eta = 100$ -1000 centipoise) and any practical spreading rate (0.1 to 1.0 cm/sec). The surface tension is generally between 30 and 50 dynes/cm and, compared to the viscosity, is a relatively minor factor.

In present aerospace bonding practice, adhesives typically are supplied as films of semi-solid resin, sometimes supported by a nylon or glass carrier cloth. Although these adhesive films are economical and convenient, their application invariably results in trapped air (Schwartz and Tegada 1972). The sequence of events is illustrated in Figure 12. When the film is first placed on the metal, regions of thin air film are trapped (Figure 12A), but as the resin softens the air agglomerates into bubbles (Figure 12B) that are displaced into the resin film (Figure 12C) if the resin meets the "wetting" criteria. Should the resin not wet the adherend, the air bubbles remain at the interface (Figure 12B). In either case, these air voids can be eliminated if the structure is bonded in an autoclave so that there is a hydrostatic pressure of a few hundred psi. In effect, the air in each void is pressurized and its volume reduced by a factor of 10 or more. Alternatively, it recently has been shown that the same effect can be accomplished by a "vacuum-release" technique (Schwartz and Tegada 1972). The structure to be bonded is placed in an oven with only enough mechanical pressure to hold the assembly together. The oven is evacuated in order to reduce the pressure of the trapped air, which is possible because at this stage the trapped air pockets are inter-connecting. The temperature is increased to a point at which resin is

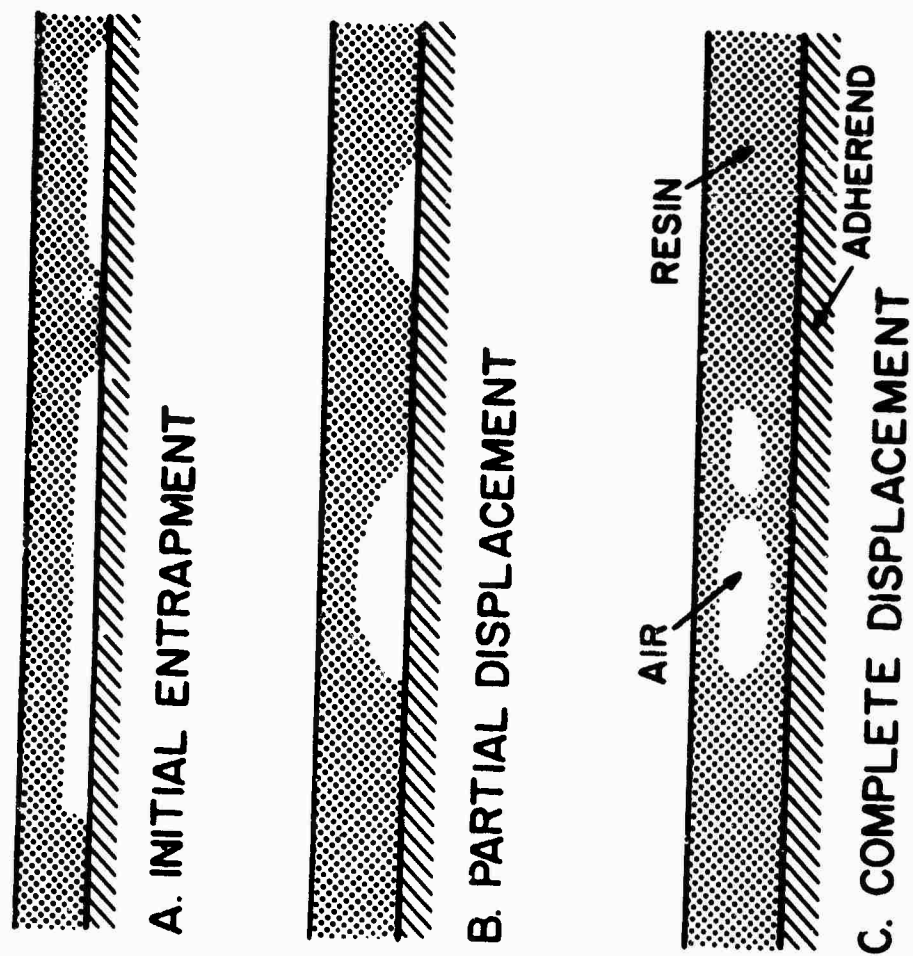


FIGURE 12 The sequence of events in air entrapment between an adherend and an adhesive resin film (Schwartz and Tegada 1972).

sufficiently fluid that when the vacuum is released the voids collapse to a negligible volume. Mechanical pressure is then applied to the assembly to squeeze excess resin out of the bond area. This technique was used to prepare void-free peel test specimens and, when compared with specimens from which the trapped air had not been removed, the void-free specimens had a greater peel strength, less tendency for unstable advance of the peel front, and greater moisture resistance (Bascom and Cottingham 1972).

#### 5.4 Adhesive/Adherend Interface

##### 5.4.1 The Interfacial Region

It is important to recognize that the adherend/adhesive interface is not a planar singularity but a region or "interphase" with properties different from the bulk adhesive (Sharpe 1972). This would be so even if the adherend were ideally smooth and chemically homogeneous and if the adhesive were a single component polymer because the molecular configuration of a polymer at an interface is different than its molecular structure in bulk (Kwei 1965). The transition from interfacial structure to bulk structure may extend over distances of hundreds or even thousands of angstroms from the interface (Lipator et al. 1971).

But adherend surfaces are never smooth or homogeneous and adhesives are seldom well defined polymers. These factors have a profound influence on the properties of the interfacial region. For example, if the adhesive fills in the surface roughness, we might consider the depth of interfacial region to be at least as great as the rugosity of the adherend surface. In addition to the gross surface roughness (e.g., machining marks), there may be a more or less porous oxide or conversion-coating layer that the adhesive penetrates to some degree.

The chemical composition of the adhesive in the interfacial region is likely to be different from the bulk because of the selective adsorption of one of the components. For example, there is evidence that in amine-cured epoxies, the amine is preferentially adsorbed by glass (Erickson 1970) and by metal substrates (Patrick et al. 1971). Enrichment of the interface with amine would cause the resin in this region to be cured differently than the bulk. Furthermore,

any excess amine left at the interface could affect the chemical phenomena associated with stress-corrosion (see Section 5.4.4). Even if there were no preferential adsorption, the adherend could still influence the solidification of the adhesive polymer. This effect is well documented in the case of polyethylene or polypropylene bonded to metals (Schonhorn 1964; Fitchman and Newman 1970), where it has been shown that, depending on the thermal conductivity of the metal, the polymer crystal structure that develops at the interface differs considerably from the bulk crystal structure (Fitchman and Newman 1970). Even in the case of amorphous, thermosetting polymers that solidify by a chemical reaction, the adherend may influence the chemical nature and/or the kinetics of the cure reaction in the immediate vicinity of the interface (Bascom 1970).

#### 5.4.2 Interfacial Stresses

The curing or solidification of the adhesive can introduce stresses of considerable magnitude throughout the bond and especially near the interface. Inter alia, these stresses result from: (a) differences in the thermal coefficients of expansion of the resin and adherend, (b) resin shrinkage accompanying the cure reaction, (c) resin crystallization, or even (d) possibly long-range orientation of the adhesive molecules. To some extent relaxation processes in the bulk resin may relieve these stresses, but near the interface the adherend will hinder relaxation by mechanical or chemical bonding restraints. The birefringence patterns seen along fibers imbedded in resins are one example of interfacial stress (Matting and Ehrenstein 1970). Also, the internal stresses at the adhesive/adherend/air line of contact can be inordinately large (Eley 1961) and visibly affect resin macrostructure (Patrick and Brown 1971). In addition to the effects just noted, interfacial stress can be induced by the roughness of the adherend. A photo-elastic study (Marian 1967) indicates that the stress pattern can be very extensive and complex.

A very critical problem in bonding is the stress that develops in trying to bond a metal to glass fiber-resin or carbon fiber-resin composite materials. For example, the thermal coefficient of expansion of aluminum (between 20 and

200 °C ) is  $24 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  for the 2024 alloy, whereas the value for a graphite-epoxy composite (between 20 and 200 °C) is  $8\text{--}10 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  transverse to the fiber direction and  $0.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  in the longitudinal direction (Geiler 1973). So large a disparity can lead to warpage or even destruction of the bond without additional loading. This topic goes beyond the interfacial aspects of bonding, and is discussed in Chapter 8.

#### 5.4.3 Crack Growth in the Interface

Failure of an adhesive joint may occur at or near the interface because of the way the structure is loaded and not because of any inherent interfacial weakness. This point is best illustrated in a study of the mixed-mode failure of "scarf" joint specimens (Trantina 1972). In this configuration (Figure 13) the bond line, BC, is at an angle to the applied load. A center-of-bond crack initiated at A will propagate perpendicular to the loading direction in an opening mode fashion until reaching the adherend, B. Then it travels along the interface, at which stage the failure is a mixture of tensile and shear modes. This mixed failure mode makes a scarf joint stronger than a simple butt joint. Indeed, a number of joint configurations incorporate the scarf bond (De Lollis 1970). This is important, because the properties of the interfacial region determine the bond strength when a failure is mechanically directed into the interface. Just how close to the interface these mechanically driven interfacial failures occur is yet to be determined. It probably will be found to be a function of the properties of the resin in this region and the stress distribution at the crack tip.

#### 5.4.4 Stress-Corrosion at the Interface

Moisture-induced failure of an adhesive bond usually occurs near the interface because of the moisture susceptibility of the metal or metal oxide and of the immediately adjacent resin (Patrick et al. 1969; Mostovoy and Ripling 1969). The magnitude of the loss in bond strength is illustrated by the data in Figure 14 taken from a study of adhesive bond fracture toughness (Ripling et al. 1971; Mostovoy and Ripling 1970). The specimen consisted of two tapered aluminum bars bonded together to form a double cantilever beam (see insert, Figure 14)

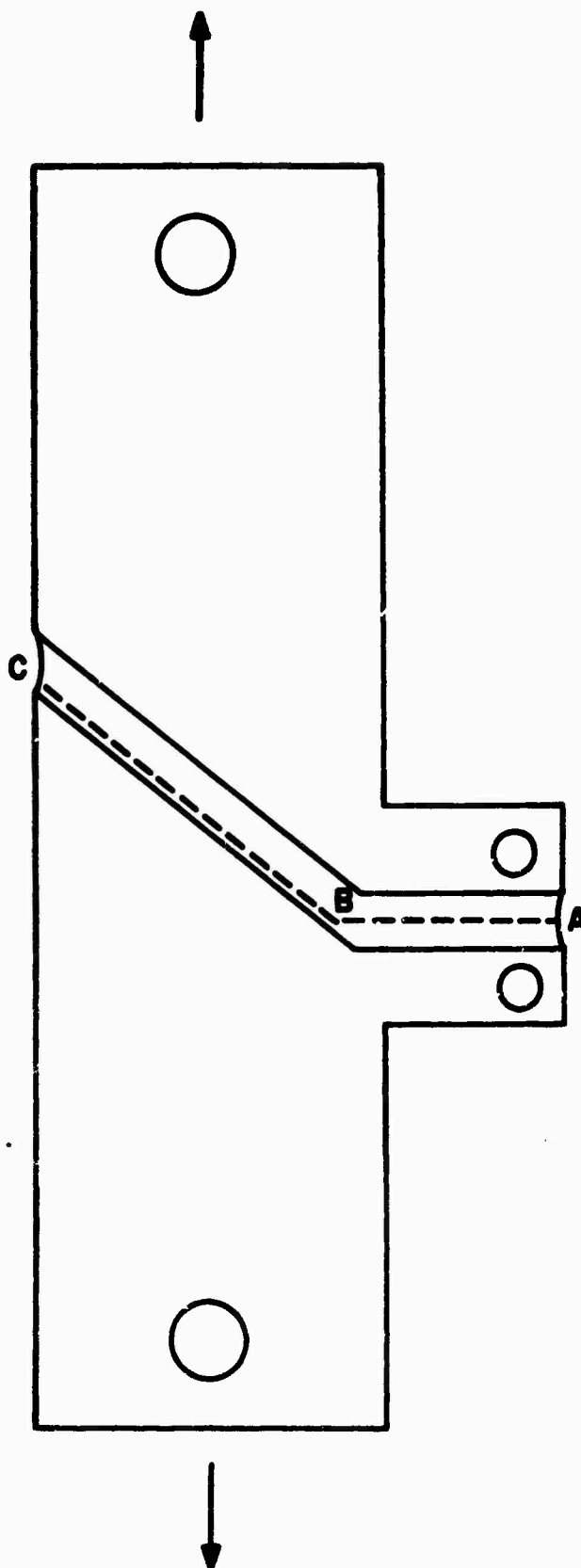


FIGURE 13 Locus of failure in an "off-axis" bond  
(adapted from Geller 1973).



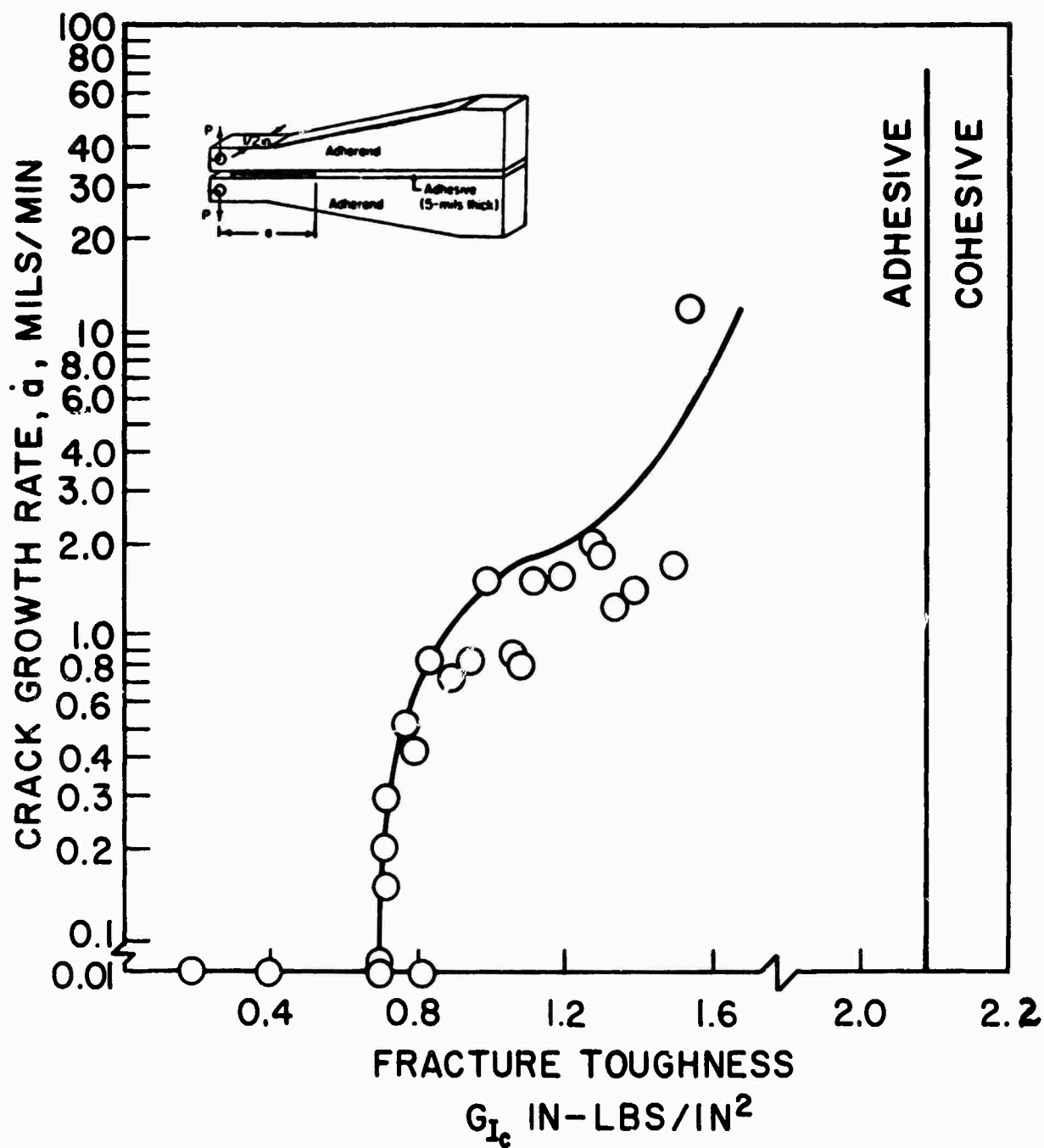


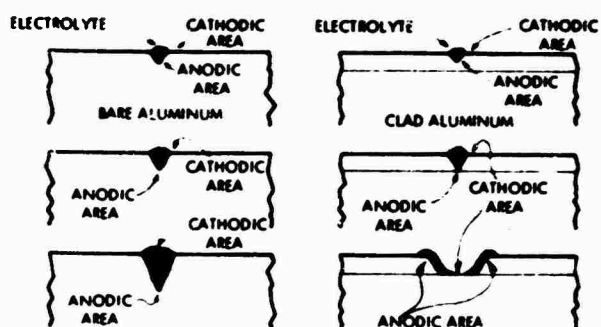
FIGURE 14 Cracking rate ( $\dot{a}$ ) vs. Fracture energy ( $G_{Ic}$ ) for a commercial adhesive-aluminum bond immersed in water of 25°C. The "dry"  $G_I$  is indicated by the vertical line separating adhesive and cohesive failure (Mostovoy and Ripling 1970),

and is loaded at the narrow end. The specimen is tapered for constant compliance so that the energy to propagate a crack,  $G_{IC}$ , is a simple function of the load,  $P$ , the modulus of the metal,  $E$ , and the beam thickness,  $b$ :

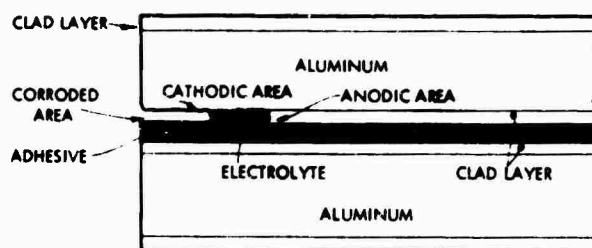
$$G_{IC} = \frac{4P^2}{b^2 E} m,$$

where  $m$  is a constant determined by the taper. The data in Figure 14 were obtained for a commercial epoxy adhesive on a nylon support cloth. A proprietary primer had been applied to the aluminum. In air at  $\sim 50$  percent RH the value of  $G_{IC}$  was  $2.08 \text{ in-lb/in}^2$ , and the failure occurred cohesively (i. e., within the center of the adhesive layer). The data points in Figure 14 were obtained with the specimen in liquid water at  $25^\circ \text{C}$ . Under these conditions failure occurred at the adhesive/aluminum interface. The sharp decline in crack growth rate,  $\dot{a}$ , with decreasing load is characteristic of all adhesives tested in this manner. The value of  $G_I$  at which this occurs,  $0.71 \text{ in-lb/in}^2$  in Figure 14, is taken as the stress corrosion fracture toughness,  $G_{SCC}$ . The difference between  $G_{IC}$  and  $G_{SCC}$  represents a threefold loss in bond toughness and is typical of the adhesives studied.

As already indicated (5.3), the chemical nature of the adherend and the adhesive resin determine the moisture susceptibility of the bond. There have been only a few diagnostic studies of moisture-induced failure. One presents evidence that stress corrosion cracking at epoxy/aluminum bonds involves a hydrolysis of the aluminum oxide (Patrick et al. 1971). Other workers argue that the moisture attacks the resin molecules near the interface (Orman 1971). The diagnostic study of the stress corrosion of bonds to titanium has been previously discussed (5.3.3). In Section 5.3.3 it was mentioned that adhesive bonds to clad metals can be especially susceptible to moisture attack. The reason for this is illustrated in Figure 15 (Weiss and Cheever 1968). A clad layer, being anodic relative to the underlying metal, corrodes sacrificially thus preventing the formation of deep surface pits (Figure 15A). However, this same process taking place at the adhesive bond leads to delamination (Figure 15B). In general, the attachment of the adhesive to a layer of metal which is anodic with respect to the rest of the metallic system is undesirable from the standpoint of corrosion



A



B

FIGURE 15 Progressive pitting of bare and clad aluminum in a corrosive environment (A) and corrosive delamination of adhesive bonded clad aluminum (B).

resistance. Note also that the chemical components in the adhesive may diffuse into the "electrolyte" area (Figure 15B) and enter into the corrosion reactions. If, for example, the adhesive is an amine-cured epoxy, any unreacted amine diffusing into the region of corrosion could affect or even control the pH of the electrolyte solution.

#### 5.4.5 Surface Primers and Adhesion Promoters

As the technology of adhesive bonding has progressed, so has the development of chemical agents for treating adherend surfaces, e.g., primers, coupling agents, and adhesion promoters. Although some rationale enters into the selection of these agents, their development has been largely empirical. Their function is to protect the adherend from moisture and other contamination prior to bonding, increase the adherend wettability by the adhesive, protect the bond from degradation by moisture, and/or improve the interfacial bond strength. These agents have been the subject of considerable study (Aker 1972; Patrick and Yager, 1971; Salomon 1967). As yet there is no fully satisfying explanation of their action. Considerable attention has been given to the so-called "coupling agents." Principal among these are the "silanes," which have the general formula  $\text{RSi}(\text{OR}')_3$  where  $\text{OR}'$  are alkoxy functions and  $-\text{R}$  is an organofunctional group ( $-\text{C}_3\text{H}_6\text{Cl}$ ,  $-\text{C}_3\text{H}_6\text{NH}_2$ , or  $-(\text{CH}_2)_3\text{OCH}_2\text{C}(\text{O})\text{CH}_2$ ). Other coupling agents include certain organo-chromium, titanate and organophosphate complexes (Patrick and Yager 1971). These adhesion promoters improve the moisture resistance of glass-to-resin and metal-to-resin bonds. They usually are applied to the adherend in such a way as to form a thin ( $<1000 \text{ \AA}$ ) polymeric film, into which the resin can penetrate and presumably interact (Bascom 1972). The fact that the adhesive resin and the primer or promoter coating can inter-diffuse implies an interfacial layer having properties considerably different than either of the components alone. This may be a key to understanding the mechanism of effective adherend surface treatment.

#### 5.5 Adhesive/filler Interface

Adhesive resins frequently are reinforced by adding inorganic powders

and/or support cloth of glass or polymer fiber. Obviously, these reinforcements augment the interfacial aspects of the bond; most of what has been said about the adhesive-adherend interfacial region is pertinent to the filler (or fiber) boundary. It can be anticipated that this boundary will be subject to attack by moisture, that the reinforcement may alter the molecular structure of the resin, and that a state of strain may exist in the resin at the interface.

Fillers are added to adhesive resins for two reasons. They increase the resin viscosity to make it easier to handle and less likely to flow out of the bond area. Cloth in an adhesive film provides support to the semisolid resin and during cure it retains the resin. Furthermore, the reinforcement is expected to improve the cohesive strength of the resin. This is a valid expectation since it has been shown both experimentally (Lange and Radford 1971) and theoretically (Lange 1970) that some filler particles can improve fracture toughness. Also, the support cloth in an adhesive film can improve bond toughness (Bascom and Cottingham 1972). In both cases the additional toughness is the result of the resin/filler interface influencing the micromechanics of failure.

#### 5.6 Problem Area Identification and Possible Solutions

There are three major problem areas in the interfacial aspects of bonding. First, the moisture sensitivity of stressed adhesive bonds indicates an urgent need for diagnostic studies in order to establish the failure mode and find corrective measures. Second, there is a need to characterize the chemical and mechanical properties of the interfacial region. And third, the knowledge that is available about the interfacial aspects of bonding is not being fully utilized. Some specifics concerning these three problem areas are outlined below.

##### 5.6.1 Moisture Induced Failure

Basic research effort on this problem should be expanded with explicit focus on identifying the mechanism of the stress-corrosion process. The problem can be attacked directly by post-failure examination of both field and laboratory specimens to try to understand the chemical nature of the process. Certainly, the analytical tools are available (see Figure 11). What is needed are ingenious

experimental approaches to examining the surfaces immediately after failure or, better still, while the presumed corrosion is taking place.

An indirect approach can be taken by examining the role of surface primers. It is known that these agents reduce the rate of bond corrosion, and if knowing how they work would greatly increase understanding of the mechanism of stress corrosion.

The payoff for advance in this problem area is obvious. The high moisture sensitivity of stressed adhesive bonds is well documented (Mostovoy and Rippling 1969; Patrick et al. 1969 and 1971; Weiss and Cheever 1968), and the field problems are very serious especially in hot, humid climates.

#### 5.6.2 Mechanical Properties of the Interfacial Region

The evidence that many joint designs fail near the interface for mechanical reasons is still fragmentary and needs further documentation. If, as seems likely, mechanically induced interfacial failure does prove to be a common phenomenon, the possibility of controlling the properties of the resin in the interfacial region should be explored.

#### 5.6.3 Improved Utilization of Research Results

Research results in any field provide guidance for technical practice. However presentation of fundamental knowledge should not be shrouded in esoteric scientific jargon but should give the practitioner meaningful and usable explanations of principles and phenomena. These principles might well be included in an adhesive handbook to assist the reader in using the handbook data.

Some specific information that should be generated and documented (if not already available) includes:

- Temperature-viscosity curves of standard adhesive formulations
- Surface composition of typical aerospace metals after standard cleaning and etching treatments
- Characterization of surface roughness imparted by etching treatments or conversion coatings on typical metals

## 5.7 Conclusions and Recommendations

### 5.7.1 Applied Research

Conclusion: There is a wealth of knowledge in surface science that is applicable to the subject of adhesives; however, no concerted effort has been made to bring this knowledge to bear on specific bonding problems. For example, the information available about metal corrosion in general has never been utilized fully in addressing the stress-corrosion of metal-resin bonds. The extensive work on the wetting and spreading of liquids on solid surfaces is only beginning to be applied to joint fabrication problems. And only recently has it been recognized that an interfacial "region" resulting from interactions between the adhesive and adherend, exists. The possibility of predicting the properties of this region are remote at this time, although these properties frequently control bond strength.

#### Recommendations.

Research in the surface aspects of adhesion must be accelerated in order to determine and then apply basic principles to the phenomena of bonding. It should be explicitly stated in funding this research that it be applied to real adhesive bonding problems and not stop with an advance in the science of surface chemistry or physics.

### 5.7.2 Surface Science and Adhesive Problem Solving

Conclusion: Some progress has been made in developing the surface aspects of adhesive bonding. However, the utilization of this information has been unduly slow.

Recommendation: The adhesive maker and user should have at least the rudiments of surface science. Also required is a cooperative continuous communication between the scientist and the practitioner. This shared knowledge should be continuously utilized in solving problems to achieve better structural bonding in aerospace applications.

### 5.7.3 Fracture Energy Criteria Research

Conclusion: Over the past several years, work has been carried out to apply fracture criteria to adhesively bonded systems. The work of Mostovoy

and Ripling has been mentioned (Patrick et al. 1969; Mostovoy and Ripling 1969; Ripling et al. 1971). These workers have refined testing techniques to a point where the method is amenable to use in commercial testing.

Unfortunately, the concept of fracture energy( $G$ ) or stress intensity, ( $K$ ) is not generally appreciated by design engineers. The lap shear data that have been accumulated over the years are generally utilized in spite of the fact that the values are essentially meaningless for structural design purposes. It is of the utmost importance that the design engineer be provided with data which are meaningful. Fracture criteria provide analyzable data from standardized test procedures. Inasmuch as the opening mode (cleavage fracture) is the most vigorous test configuration, it is only necessary to obtain opening mode data; it is not required that shear and torsion values be found.

Determination of  $G_c$  (critical strain energy release rate) can be readily utilized as a quality assurance test procedure. The method is most sensitive to processing and product variables and has great potential as an effective method for characterizing an adhesive system.

Recommendations: It is recommended that the currently available experimental techniques for determination of fracture energy criteria, as applied to adhesive bonding, be extracted from scattered literature, develop standardized tests and published by a recognized agency, such as the American Society for Testing and Materials, so that these techniques can be readily understood and used more extensively and so that a useful body of technical data from such methods can be developed for use by designers in the adhesive bonding phases of aerospace hardware fabrication.

It is strongly recommended that additional research concerning fracture energy criteria be funded in order that meaningful data for design use are generated. It is further recommended that an instructional team be established for the purpose of informing designers and technologists of the value of the fracture energy criteria design.



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## CHAPTER 6

### MANUFACTURING AND PROCESSING

#### 6.1 Purpose

The purpose of this chapter is to identify problem areas directly associated with the production of a bonded structure and to recommend possible solutions. Only those problems specific to the production sequence are included.

#### 6.2 State of the Art

##### 6.2.1 Introduction

Adhesive bonding of metal aircraft structures began in the mid-1940s and has been increasing gradually since that time. Both sandwich and metal-to-metal bonded applications have evolved. Adhesive bonding and the sandwich concept are closely associated, and each technology has exerted its influence on the other. Since practically all sandwich panels contain metal-to-metal joints, processing procedures and adhesive formulations represent a compromise designed to best adapt a single adhesive system to both types of joint. Generally it is impractical to use different adhesive systems in the same part.

##### 6.2.2 Process Definition

In heat-cured adhesive joints, the basic process which forms the finished joint requires for a period of time the controlled heating of the adhesive while in contact with the surfaces to be joined. The heat cycle cures the adhesive. Pressure is needed to bring the two surfaces close together. During the cure cycle the adhesive must liquefy in order to insure proper wetting and flow. During the liquid phase some adhesive must be squeezed out in order to wash out trapped air and to insure the thin, uniform bond-line needed for optimum properties. The basic requirements of heat and pressure for a predetermined time dictate the processing procedures required. For room-temperature curing systems no heat is needed. For convenience, the production of bonded structures can be considered in terms of nonrecurring and recurring steps required to produce each part.

### 6.2.2.1 Nonrecurring Process Steps

Certain nonrecurring steps are required to make the overall process successful. Although some of these steps are treated in detail elsewhere in this report and, hence, are outside the scope of this chapter, those portions that have a direct impact on the manufacturing process are considered within this chapter's scope are:

Structural Design - The process of defining structural configuration and materials of construction such that desired performance is achieved

Manufacturing Plan - Definition of processing procedures, materials acceptance criteria, tooling philosophy, process control procedures, and finished part inspection criteria. The plan is implemented through a series of specifications and manufacturing instructions

Tool Design, Fabrication and Qualification - Production of the tool family needed to produce the part

Repair Procedures - Procedures for repair or rejected parts that can be reworked into acceptable condition

### 6.2.2.2 Recurring Process Steps

Recurring steps are those required each time individual bonded assembly is fabricated and include the following:

Detail Preparation - A bonded assembly consists of many individual parts of various sizes and shapes that collectively make up the finished part. These individual parts are called details and include skins, honeycomb (or other) core, doublers, edge member closeouts, inserts, brackets, etc. Each detail must be cut, shaped, and inspected to ensure proper fit. Adhesive primer is frequently applied, usually by spraying, followed by air or oven drying to remove solvent. In some instances, the adhesive may be applied directly to the skin or core using hot melt or solution coating techniques. The details are now ready for assembly.

**Assembly** - This step (commonly called "lay-up") involves the assembly in proper order, on a suitable tool, of various details plus adhesives and the proper preparation of the assembly for the curing process. Unless the adhesive is included in the assembly as a dry or slightly tacky film. In a few instances, paste adhesives are used but application costs generally are excessive unless special application devices are available. When required, specially formulated paste potting compounds are injected into core areas where hard points are needed for mechanical attachments. With all the details properly assembled on the tool, an autoclave cure lay-up requires sufficient bleeder cloth to ensure proper evacuation of the assembly plus a suitable bag material to transmit the autoclave pressure to the part. For a press cure, or for special curing fixtures, other special devices may be required in the lay-up.

**Cure** - Most bonded aerospace structures are cured in autoclaves that operate at pressures to 200 psi and temperatures up to 260°C or more. An inert gas (nitrogen or carbon dioxide) atmosphere is usually used to obviate hazard of fire. Autoclaves are best suited to curing large curved panels. Small, relatively flat panels frequently are cured in large heated flat platen presses that are faster than autoclaves because of more direct heat transfer. Some assemblies, especially for long production runs, are specially tooled, using heating blocks, plus spring, clamp, or hydraulically actuated pressure bars or plates. In some cases, heated tools are used in an unheated autoclave, especially where cure temperatures exceed the capability of the autoclave.

For some applications involving low loads on the bond-line, rivet bonding is used. In this technique, the two parts are cleaned, assembled with adhesive, and riveted together. This assembly is then oven-cured, without any additional pressure. In weld bonding, the assembly, including adhesive, is spot welded (through the adhesive) and cured as in rivet bonding. An alternate procedure is to spot weld the details together and apply a low viscosity adhesive at the edge of

the overlap. Upon heating (if needed to cure the adhesive) capillary forces draw the adhesive into the bond line where it cures to form the weldbond. Room-temperature curing adhesives are not used very frequently due to the low load bearing quality of the joint. Cocuring is a technique used for simultaneously curing a fiber-reinforced plastic laminate and bonding it to another detail, either another laminate, a metal, or honeycomb core. A separate adhesive or the excess resin squeezed out of the laminate during cure may serve as the bonding agent.

Post-Bond Operations - Most structures require some clean-up of excess adhesive, edge trim, and, in some instances, machining for attach points, etc.

Inspection - Each part must be inspected for compliance with established requirements. Generally inspection covers dimensions plus visual inspection for obvious voids, detail slippage, or other gross flaws. In addition, process control coupons are frequently run with the part and are destructively tested to verify proper cleaning and cure cycle. In some instances, the part is designed with a trim section that is cut off and tested destructively. Leak tests also may be carried out to prove that the part is sealed.

Some form of nondestructive testing is almost always applied to bonded structures. The most commonly used procedures are based on ultrasonics and x-ray examination. Simple bond testers with hand-held probes and visual indication of deviation from pre-established standards frequently are used. For more extensive testing, ultrasonic "C" scan, which provides a printed record of the test, is used (Fehrle 1971). Mismatch of details, core splices, etc., are revealed by x-ray. Holographic interferometry has been used for certain large panels (Wells 1969) and is more rapid than "C" scan. Thermal conductivity methods sometimes are used, either by a scanning technique using a radiation thermometer pickup (Kaplan 1972) or by observing visual color changes produced chemically in applied coatings (Brown 1972; Allinikon 1971). In liquid crystal techniques, color patterns are produced when special compounds coated on the part are heated to

their melting point. Reusable plastic films containing encapsulated liquid crystal compounds are now available to reduce the cost of this technique.

### 6.2.3 Problem Areas

Although there are many shortcomings and problem areas associated with adhesive bonding, those most closely linked with manufacturing are:

- a. Making full-scale parts under production conditions of the quality obtained in simple test panels fabricated under laboratory conditions
- b. Obtaining consistent quality from part-to-part and within each part
- c. Achieving minimum cost consistent with a and b above

Each of the specific problem areas defined in the following section have a significant influence on one or more of the above general problems, and the possible solutions suggested are designed to minimize or eliminate the problem areas.

## 6.3 Identification of Problem Areas

This section defines specific problem areas associated with each step in the manufacturing sequence.

### 6.3.1 Nonrecurring Process Steps

The following specific problem areas fall within the nonrecurring portions of the processing cycle, as previously defined.

#### 6.3.1.1 Design

Structural design is treated in detail in Chapter 8; however, the producibility of a part and the interaction between design engineer and manufacturing engineer is considered a proper subject for this chapter.

Producibility of the design is one of the major factors essential to the successful production of high-quality, low-cost bonded structures. It is the opinion of the Committee that a significant portion of the poor quality observed in bonded structures could have been prevented if the technology available when the part was designed had been applied. Poor joint design, improper definition of



tolerances, and the wrong choice of adhesives are some of the reasons for inconsistent quality. Limited durability in corrosive environments frequently is the result of a lack of understanding of the factors that control corrosion.

One must consider the compatibility of materials of construction with manufacturing processes and environment, i.e., the basic compatibility of a part produced of a particular material by a certain technique. For example, a sand cast aluminum part which is to be bonded and the assembly must resist hot humid exposure; however, the alloy usually is high in silica and may not lend itself to FPL etch along with other aluminum components, the part may be porous, and the sand may be contaminated with silicones. Similarly, an aluminum alloy upon heat treating becomes very sensitive to stress corrosion due to residual amine from epoxy resin adhesive. Also, a sheet stock may have its surface smeared in a punch press; this yields a weak boundary layer not removed in etching; drilling or machining would not create this problem.

#### 6.3.1.2 Manufacturing Plan

The manufacturing plan is documented through a series of processing specifications, process control procedures, and detailed manufacturing procedures. Historically, most companies have written their own process specifications; each one differs from the others in many significant details. For example, the chromic/sulfuric acid etch for cleaning aluminum was developed more than 20 years ago and is essentially standard in industry; however, most companies employ their own variant in either solution concentration or process time/temperature and, hence, each process specification is different.

#### 6.3.1.3 Tooling

Tool design and fabrication is a major portion of the cost of the non-recurring portion of the manufacturing sequence. In addition, improper design results in poor quality and uniformity. The tooling philosophy is determined by the number of required parts, the nature of the materials selected, and the design configuration. The temperature, time, and pressure conditions required for curing the adhesive strongly influence tool cost and performance. Any basic improvement or

simplification in processability of the adhesive system will have a direct and favorable impact on the tooling requirements.

#### 6.3.1.4 Repair Procedures

Definition of shop and field repair procedures is a part of the manufacturing plan. Rework of manufacturing defects sometimes is a practical procedure to reduce scrap rates; it can have a significant impact on manufacturing costs. However, current repair procedures are too expensive. It is generally difficult to rebond a damaged area in a bonded assembly with the same adhesive systems used for the original bond. The surface of the part generally cannot be recleaned by the original process, and application of the optimum heat/pressure/temperature cycle may not be possible. This problem is especially severe when field repair is necessary.

#### 6.3.2 Recurring Process Steps

Those processing steps that recur for each part manufactured were defined above and are: detail preparation, assembly, cure, post-bond operations, and inspection. Problem areas specific to each step are outlined below.

##### 6.3.2.1 Detail Preparation

Once the design has been fixed, the shape and size of each detail is established and the manufacturing engineer must define the manner in which each detail is prepared. Improper processing prior to bonding may degrade joint strength. For example, certain lots of titanium sheet are unbondable in spite of careful application of standard surface treatments. Cast aluminum details sometimes will not respond properly to cleaning solutions, causing low-strength joints. Improperly formed or hot-sized parts sometimes distort during the cure cycle, producing improper fit or bond-line tolerance. The cutting of advanced composite details, either cured or in the B-stage, sometimes is a problem. Boron composites, particularly boron/titanium combinations, are especially difficult to machine.

##### 6.3.2.2 Assembly

After all details are prepared for bonding, the lay-up procedure is

started. In complex parts, various subassemblies may be required, and only simple parts are cured in a single step. Most adhesives currently in use are in film form. They are applied by hand fitting tailored sheets to the core and metal details as they are assembled. This process is a slow, costly hand labor operation. For advanced composite structures, the lay-up of the composite material is almost always the most expensive portion of the manufacturing process. Considerable effort has been expended on tape laying machinery, but deposition rates of only a few pounds per hour are being achieved; hence, costs are excessive. Skins are frequently laid up, cured, and then assembled and bonded to produce the structure. Sometimes, several cure cycles are required.

#### 6.3.2.3 Cure

With sufficient pressure to hold the parts in contact, heat is applied until the adhesive melts, flows, and cures. Cooldown, under pressure, generally is required. The entire cure cycle is slow, costly, and unreliable. In order to achieve optimum properties with currently available systems, autoclave or press pressure is required. Cure cycles frequently require four or five hours due to the poor heat transfer and large tool mass. In addition to the time required, thermal gradients frequently introduce stresses in the joint. Even if uniform temperatures are maintained, subsequent cooling produces stresses in the joint.

#### 6.3.2.4 Post-Bond Operations

These procedures include clean up, trim, and installation of fasteners. The durability of bonded panels may be influenced by the manner in which the post-bond machining is carried out. Although there is no visual evidence that micro-cracks which can serve as failure initiation sites are created during machining,\* the possibility exists and may be a contributing factor to poor quality or premature failure. In boron fiber reinforced composite structures, the machining of the composite material, especially combinations of composite and metal, is difficult, slow, and costly.

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\* But see Shane, "On the Lap Joint Shear Test", ASTM-STP 289 - Symposium on Shear and Torsion Testing (1960), 56 ff, for evidence of machine damage to bonded joints.

#### 6.3.2.5 Inspection

The final step in the manufacturing process is inspection to prove that each part meets established requirements. The detection of substandard bonds is an unsolved problem, and lack of reliable nondestructive inspection procedures for void detection is a major reason for limited confidence in structural adhesive bonding. Many of the more effective methods for detecting bond-line voids are expensive. Ultrasonic inspection, one of the best inspection methods, is a relatively expensive procedure since it requires a slow detailed scanning of the entire surface. Complex shapes obviously complicate this problem.

#### 6.4 Identification of Possible Solutions

In this section, a series of recommended solutions to each of the problem areas outlined in paragraphs 6.3.1 - 6.3.2 are presented.

##### 6.4.1 Nonrecurring Processing Steps

##### 6.4.1.1 Design Recommendations

##### 6.4.1.1.1 Adhesive Bonding Handbook

A comprehensive handbook on all aspects of adhesive bonding techniques should be prepared. This book should include material properties, joint design and analysis, tooling concepts, manufacturing costs, environmental resistance, etc., and perhaps should be patterned after the Metals Handbook sponsored by the American Society of Metals. This handbook must be kept up to date in view of changing technology.

##### 6.4.1.1.2 Instruction Team

An instructional team of well qualified engineers and scientists should be established to prepare a detailed instructional and review program on the design of adhesive-bonded structures. After preparation of a complete presentation, this team should tour the facilities of the various aerospace contractors and subcontractors throughout the country, presenting a short course on adhesive-bonded concepts and offering advice and consultation on specific problems.

##### 6.4.1.1.3 Technical Meetings

Every effort should be made to encourage interdisciplinary participation in meetings of professional societies where adhesive bonding is discussed.

Government contractors should be encouraged to send design engineers to adhesive bonding symposia; likewise, materials and process engineers specializing in adhesive bonding should be encouraged to participate in structural design oriented conferences. In addition, professional societies, such as the Society for the Advancement of Materials and Process Engineering, American Society for Testing and Materials, or Society of Automotive Engineers should be encouraged to present national conferences on the design/manufacturing interface for bonded structures.

#### **6.4.1.1.4 Formal Education**

Encouragement and assistance should be given engineering departments in colleges to broaden the scope of their instructional program to include a more thorough coverage of adhesive bonding technology in the materials engineering curriculum.

#### **6.4.1.2 Manufacturing Plan Recommendations**

##### **6.4.1.2.1 Uniform Specifications**

An effort should be made to standardize specifications governing the bonding process. Similar process procedures for specific adhesive types should be consolidated into a single set of procedures for general industry use. In order to ensure general acceptance by buyer and seller, sufficient test data may be required to establish the performance of the selected procedure.

#### **6.4.1.3 Tooling Recommendations**

##### **6.4.1.3.1 Weld Bonding**

One of the simplest ways to minimize tooling for adhesive bonding is to extend and broaden the weld bonding technique. This procedure fixes the assembly to be bonded in its desired configuration by spotwelding, hence, greatly simplifying requirements for support during cure. It is recommended that improvements in this technology continue to be supported.

##### **6.4.1.3.2 Increased Adhesive Toughness**

Most adhesive systems intended for high-temperature service are relatively brittle and subject to edge and corner damage after bonding. Drill fixtures and holding jigs for riveting must be very accurate in order to guard

against any possible bond-line damage during assembly. Exposed corners of partially bonded assemblies must be protected from accidental damage during the post-bond operations. New adhesives with increased toughness should be developed in order to minimize this problem. In addition, such tougher systems should perform better under actual service stresses.

#### 6.4.1.3.3 Low Temperature Cure Systems

Adhesive systems that cure at temperatures in the range of 120°C present fewer tooling problems than higher temperature curing systems. Problems of different coefficients of expansion of the tool and bonded assembly are less troublesome. This factor is especially significant with graphite composites due to their very low coefficient of expansion in the fiber direction, as compared to metals. Problems of dimensional change due to different materials in the structure are less complex from the tooling standpoint. There is a thermal gradient problem resulting from the heat sink effect of a large tool. This may result in curing the assembly with some details hotter than others; hence, the part will have built-in stresses when cooled to room temperature. This problem is minimized as cure temperature decreases.

#### 6.4.1.4 Repair Recommendations

##### 6.4.1.4.1 Room-Temperature Curing Adhesive

A research program should be instituted to develop an adhesive system that produces a high-quality bond at ambient cure temperatures and limited pressures. This would greatly facilitate repair and rework. The target system must have sufficient durability to provide confidence that repaired parts will provide the same or nearly the same performance as the original production joint.

#### 6.4.2 Recurring Processing Steps

##### 6.4.2.1 Detail Preparation Recommendations

###### 6.4.2.1.1 Process Control

More basic information is needed on the effect of various metal processing procedures on surfaces to be bonded. Rolling mill lubricants, release agents, cutting oils, sand molds for castings, and the like which are compatible

with existing bonding processes must be defined. Substitute processes must be developed, or improved adhesives and/or adhesive processing procedures must be developed where compatibility does not reliably exist.

#### 6.4.2.1.2 Forming Methods

A better understanding is needed of the role of detail shape changes in stress relaxation during the cure cycle. The amount of built-in stress that can be tolerated for various metals should be defined so that hot sizing of details is specified only when needed.

#### 6.4.2.1.3 Cocuring

Whenever possible, advanced composite design should preclude the requirement for separate composite details by calling out the use of cocuring of composite and structure; the cocuring concept should continue to be supported.

#### 6.4.2.4 B-Stage\* Forming

Normally, advanced composite skins are produced by laminating together a series of single plies laid up one layer at a time on a tool of the desired shape. It has been shown recently, however, that several plies of B-stage material can be laid up on a flat tool and, prior to cure, formed over a contoured tool. This process has been called B-Stage forming and offers a significant cost savings potential. However, its limitations, in terms of number of plies that can be formed about a given radius, and the conditions for forming, in terms of resin flow, rate, temperature, and compaction, need to be defined.

#### 6.4.2.1.5 Surface Treatment, Metal

The choice and use of metal surface treatments prior to bonding is still a problem, despite many years of effort in this area, and is considered in detail elsewhere in this report. From the processing standpoint, nonuniformity in the industry already has been identified. In addition, less complex (hence less expensive) procedures for preparing metal surfaces of various types are required. Surface treatments suitable for field repair are needed. Titanium surface treat-

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\* B - Stage is a term applied to a partially-cured but still thermoplastic resin that becomes thermoset on full cure.

ment procedures should be emphasized.

#### 6.4.2.1.6 Surface Treatments, Composites

The surface treatment of advanced composites generally is accomplished through use of a peel ply, generally woven glass or nylon, that is laminated to the surface when the laminate is cured and is peeled off just prior to bonding. This procedure supposedly exposes a freshly fractured resin surface, suitable for immediate bonding without any additional treatment. However, recent work has shown that certain types of peel plies degrade resultant joint strength of the bond. Others are difficult to remove and may damage the outer ply of the laminate. The peel ply surface treatment technique should be developed further through the definition of optimum material and weave for easiest removal and best bond strength.

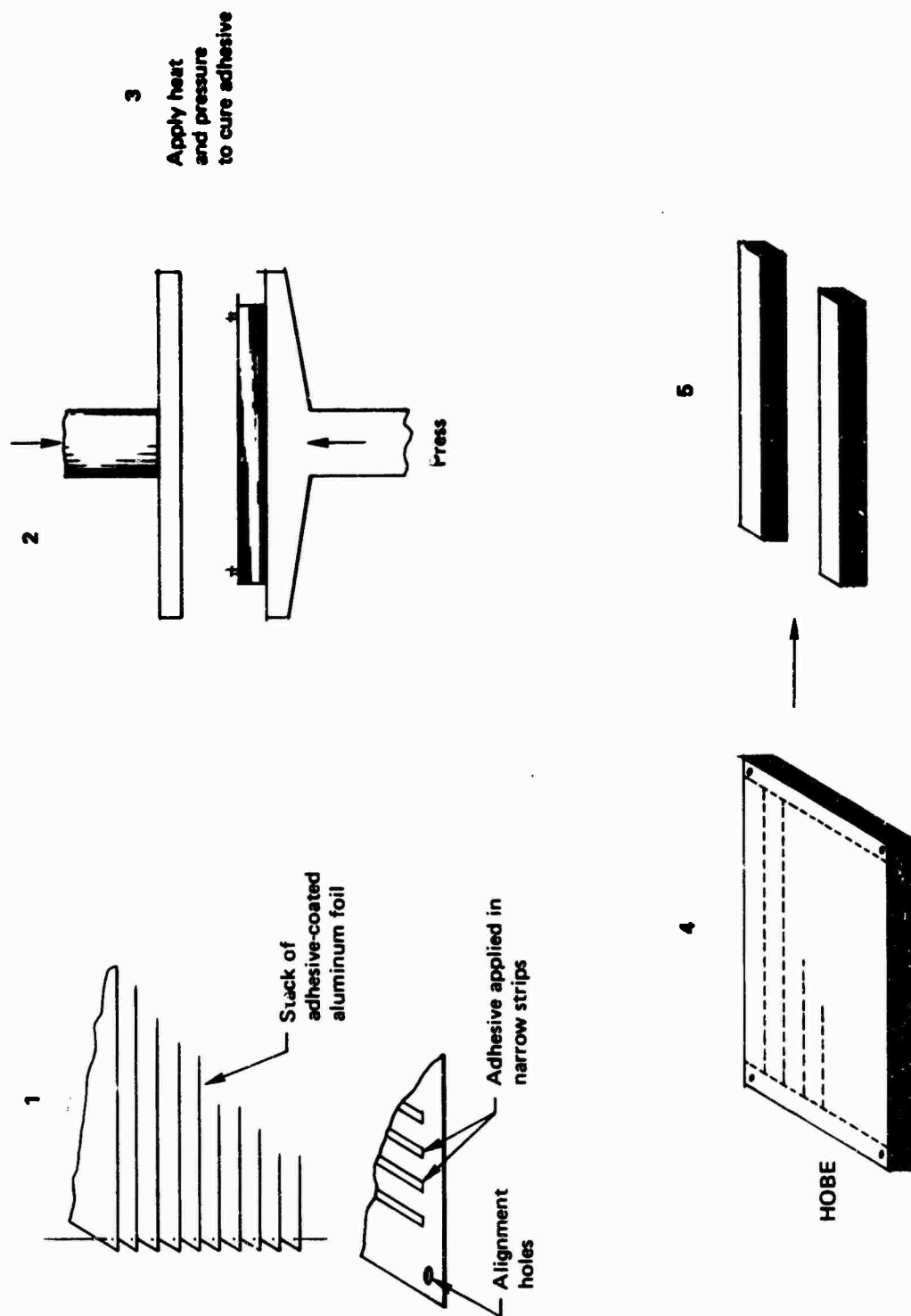
#### 6.4.2.1.7 Core Machining

The machining of honeycomb core to the required taper or contour frequently is an expensive and time consuming procedure. As a low-cost substitute, metal core sometimes is crushed to the desired shape, but this procedure is questionable from the standpoint of fatigue strength and core shear strength. Test data to define the performance characteristics of crushed edge core sandwich panels would allow more extensive use of this low-cost manufacturing technique.

#### 6.4.2.1.8 Node Bond Adhesive

Aluminum foil honeycomb core is manufactured by a process that consists of applying suitably spaced parallel strips of node bond adhesive to sheets of cleaned aluminum foil. These sheets are stacked up in a pile and held in position by pins through indexing holes around the edges of each sheet. Heat and pressure are applied to cure the adhesive. The resulting assembly, called a HOBE, (Figure 16), is converted into honeycomb core by a process called expansion (Figure 17). In this process, rods are inserted in the unbonded gaps between the bonded nodes, inside the top and bottom plies only, and the hobe is uniformly stretched. The unbonded areas between each node bond deform to produce





After cure, trim and slice to desired thickness

FIGURE 16 Aluminum honeycomb core HOBE manufacture.

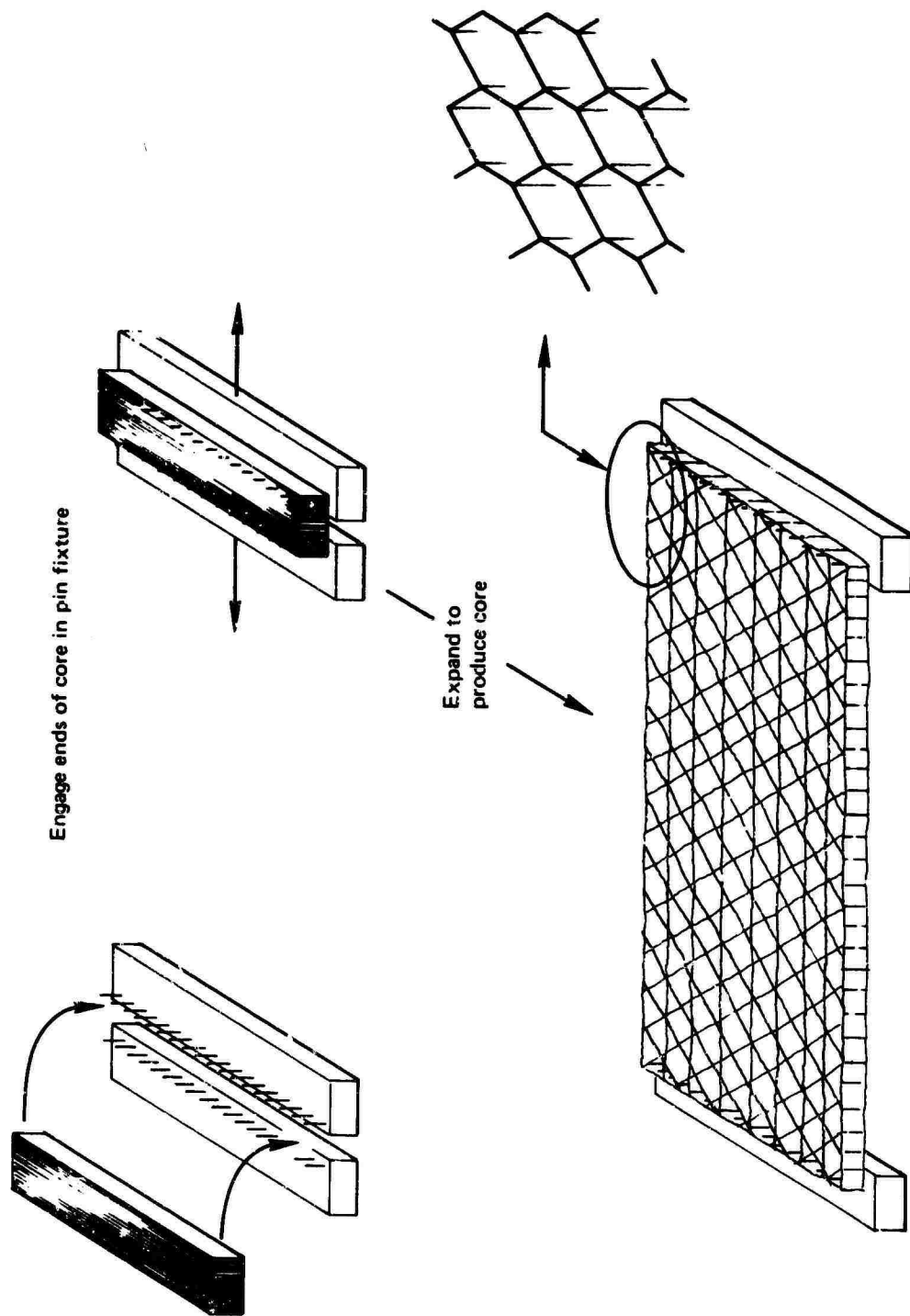


FIGURE 17 Expansion of HOBEL to produce core.

the familiar hexagonal core structure. Core expansion may be the only instance where an adhesive is stressed in true peel, since the node bonds must resist peeling and deform the foil to the required shape. This process is workable with standard thicknesses of 5052 or 5056 aluminum alloy. However, the 2000 series aluminum alloys with higher yield strength are barred from expansion, except for very thin foils, because the available adhesives fail in peel without deforming the foil. Where weight savings considerations require the use of high-strength core, the individual core strips must be preformed to the necessary shape, with adhesive applied at the nodes, and bonded in the expanded position. This step requires a hexagonal shaped removable rod in each cell to transmit pressure. Core manufactured by this technique is much more expensive than core manufactured in the hob. Also, due to its low density in the expanded form, such cores are bulky and expensive to ship and store.

Because of its high cost, 2000 series core in a sandwich structure is specified only for those areas where it is structurally required; the cheaper, lower-strength hob type is spliced in where it will carry the necessary loads. However, building up a core by splicing together separate pieces is expensive, and the core splice adhesive adds to the part weight.

The availability of high peel resistant adhesive that would make it possible to expand high-strength aluminum alloys and would result in a significant cost savings should be sought.

#### 6.4.2.2 Assembly Recommendations

##### 6.4.2.2.1 Bulk Adhesive Application

More emphasis should be placed on bulk adhesive systems (hot melt-able solids, liquids, or powders) that can be applied directly to details by simple mechanical means. Both materials formulations and processing procedures need further development.

##### 6.4.2.2.2 Cocuring

Cocuring technology should continue to be supported. In addition, lay-up procedures that are more rapid and efficient than the mechanical lay-up of

3-inch wide tape should be developed.

**6.4.2.3     Curing Recommendations**

**6.4.2.3.1   Low Temperature Cure Adhesives**

Simple low-pressure, low-temperature cure adhesive systems need to be developed. Self-heated tooling that need not be moved into an autoclave for pressure and heating needs to be developed. Systems such as thermoplastics that do not require cure or that cure very rapidly, perhaps by some form of radiation, would decrease costs.

**6.4.2.4     Post-Bond Operations Recommendations**

**6.4.2.4.1   Composite Machining**

Development of better machining techniques for boron composite structures should be continued. In addition, design concepts that eliminate or reduce machining requirements should be encouraged.

**6.4.2.4.2   Machining Damage**

The influence of machining on joint quality should be determined and proper machining techniques defined. The significance of microcracks as related to fracture mechanics should receive special attention as should the role of microcracks on durability.

**6.4.2.5     Inspection Recommendations**

**6.4.2.5.1   Low Bond Strength Joint Detection**

Any promising leads in this area should be encouraged. Some promising results have been achieved with acoustic emission, but few test data are available. Some claims have been made for certain ultrasonic methods, but no proven procedures are available.

**6.4.2.5.2   Low-Cost Nondestructive Inspection.**

Low-cost, rapid inspection methods that reveal unbonded areas need to be further developed. Techniques capable of inspecting the entire part or a large area of the part in one operation are needed; examples are laser and ultrasonic holography. Electronic enhancement of X-ray images appears to offer promise. Exoelectron emission also should be explored.

## 6.5 Priorities

This section defines the relative importance of each problem area. In establishing these priorities, it was recognized that there are several interacting factors whose sum establishes the relative merit of each recommendation. In order to arrive at a best judgment on each recommendation, the Committee used an arbitrary rating system. Each recommendation was rated on four criteria: practicality, cost reduction impact, quality improvement, and development cost. Practicality was considered as an assessment of the chances of success in achieving each technical objective. A high degree of confidence was rated as 10 and a low, as 0. A similar scale was used to rate cost reduction impact and quality improvement. Development cost, i. e., cost to carry out the recommendation, was rated as 10 for an inexpensive effort and 0 for a very expensive effort. Each of the 22 recommendations was rated and the total points, the relative ranking, and the spread, measured as a percent of the top score were recorded. These data are contained in Figure 18 and Figure 19 lists the same items rearranged into priority order. This rating system was adaptable to the subject matter of this chapter, because of the availability of reasonable judgments on manufacturing and processing techniques on a practical basis within the Committee. This rating system could not be effectively used in other chapters. The following specific conclusions are recorded.

### 6.5.1 Nonrecurring Processing Steps

#### 6.5.1.1 Design Recommendations

The adhesive bonding handbook was rated as the most significant item and, hence, has the highest priority. The instruction team and technical society symposium recommendations also rated high (97 percent of best ratings). All three of these items were considered to be relatively inexpensive, with substantial payoff in both cost and quality factors. The formal education factor was rated somewhat lower because of uncertainties in the practicality factor and a less assured payoff than the other design items.

#### 6.5.1.2 Manufacturing Plan Recommendations

Uniform specifications recommendation -- This item was rated low because of limited cost and quality improvement factors.

#### 6.5.1.3 Tooling Recommendations

In this area, weld bonding development rated highest, partly due to its advanced status; hence, a limited additional investment should insure good results. Both low-temperature curing systems and increased toughness systems rated low.

#### 6.5.1.4 Repair Procedures Recommendations

The development of low-temperature curing systems was rated relatively high, partly due to the significant improvement potential over the systems now available.

#### 6.5.2 Recurring Process Procedures

##### 6.5.2.1 Detail Preparation Recommendations

Seven of the 22 recommendations fell in this area, with the process control, node bond adhesive, and stage forming of composites being highest rated. Major factors were cost and quality. The other four items -- forming methods, (metals) cocuring, surface preparation, and core machining -- were lower rated.

##### 6.5.2.2 Assembly Recommendation

The bulk adhesive development item was rated relatively high due to both cost and quality improvement factors.

##### 6.5.2.3 Cure Recommendation

The development of a low-temperature curing system received a fairly low rating, due partly to limited potential for quality improvement by anticipated available technology.

##### 6.5.2.4 Post-Bond Recommendations

The composite machining recommendation was well-rated due to relatively good payoff potential. The machining recommendations were rated fairly low due to limited cost reduction potential.

#### 6.5.2.5 Inspection Recommendations

Substandard joint detection was rated low, mainly due to low potential chances of success and high cost to implement. Low-cost nondestructive test development was rated moderately high due to good payoff potential.

#### 6.6 Estimate of Benefits

Each of the recommended projects will require time and effort for successful implementation. Figure 18 contains a relative estimate of costs and also a relative estimate of payoff potential in terms of cost reduction or enhanced performance obtainable by successful implementation of each program. Figure 19 shows recommended programs arranged in order of priority. In this section of the report, some semi-quantitative estimates of these potential benefits are presented.

##### 6.6.1 General

As previously pointed out, both nonrecurring and recurring costs are appropriate to the total cost picture. The nonrecurring costs are very high compared to the average cost to produce a single unit. However, once methods are established, experience is gained, and production quantities are involved, the nonrecurring costs quickly lose most of their significance. Figure 20 illustrates this relationship for an idealized circumstance where the ratio of nonrecurring costs drop rapidly, and after 50 production units, the major costs are the recurring ones. Thus, it can be seen that cost reduction programs directed to the recurring cost area will have a much greater impact than those directed to non-recurring costs, unless short production runs are involved. For this discussion, it has been assumed that production quantities are the major consideration and no recommendations designed specifically to reduce nonrecurring costs have been presented. It is obvious, however, that actions taken in the nonrecurring area can have a significant influence on both performance and recurring costs; hence, certain recommendations in the nonrecurring area are included.

##### 6.6.2 Definition of Benefits

The most direct and obvious benefits obtainable through processing-

RECOMMENDED APPROACH			Practicality	Cost Reduction	Quality Improvement	Impact	Development Costs	TOTAL	RANKING	% of #1
1	Design	- Adhesive Bonding Handbook	8	8	8	5	29	1	100	
2		- Instructional Team	8	6	7	7	28	2	97	
3		- Technical Meetings	7	5	7	9	28	2	97	
4		- Formal Education	5	6	7	8	21	6	72	
5	Manuf. Plan	- Uniform Specifications	7	2	1	9	19	7	65	
6	Tooling	- Weldbonding	8	4	5	5	23	4	79	
7		- Tough High Temperature Adhesive	3	3	8	3	17	9	59	
8		- Low Temp. Curing Adhesive	6	5	2	4	17	9	59	
9	Repair	- Low Temp. Curing Adhesive	4	8	7	5	24	3	82	
10	Detail Prep.	- Process Control	7	5	7	4	23	4	79	
11		- Forming Methods	7	1	3	7	18	8	62	
12		- Cocuring	7	7	0	3	17	9	59	
13		- Stage Forming	6	8	0	7	21	6	72	
14		- Surface Preparation	3	4	2	5	14	12	48	
15		- Core Machining	3	5	0	7	15	11	52	
16		- Node Bond Adhesive	4	6	2	5	17	9	59	
17	Assembly	- Bulk Adhesive Development	6	7	5	5	23	4	79	
18	Cure	- Low Temp. Curing Adhesive	4	8	2	4	18	8	62	
19	Post Bond	- Machining of Composites	5	5	5	6	21	6	72	
20		- Machining Damage	2	0	7	7	16	10	55	
21	Inspection	- Substandard Joint NDI	2	2	8	2	14	12	48	
22		- Low Cost NDI	6	8	3	5	22	5	76	

FIGURE 18 Rating sheet -- recommended programs.



		Total Points	Ranking	% of #1	Priority
1	Adhesive Bonding Handbook	29	1	100	
2	Instructional Team	28	2	97	
3	Technical Meetings	28	2	97	
4	Low Temperature Curing Adhesive (Field Repair)	24	3	82	A
5	Process Controls (Detail Preparation)	23	4	79	
6	Weldbonding	23	4	79	
7	Bulk Adhesive Development	23	4	79	
8	Low Cost NDI	22	5	76	
9	Formal Education	21	6	72	
10	Machining of Composites	21	6	72	
11	Stage Forming	21	6	72	B
12	Uniform Specifications	19	7	65	
13	Low Temp. Curing Adhesive (Cure Cycle)	18	8	62	
14	Forming Methods	18	8	62	
15	Node Bond Adhesive	17	9	59	
16	Tough High Temperature Adhesive	17	9	59	
17	Low Temp. Curing Adhesive (Tooling)	17	9	59	
18	Cocuring	17	9	59	C
19	Machining Damage	16	10	55	
20	Core Machining	15	11	52	
21	Surface Preparation	14	12	48	
22	Substandard Joint NDI	14	12	48	

FIGURE 19 Recommended programs ranked in priority order.

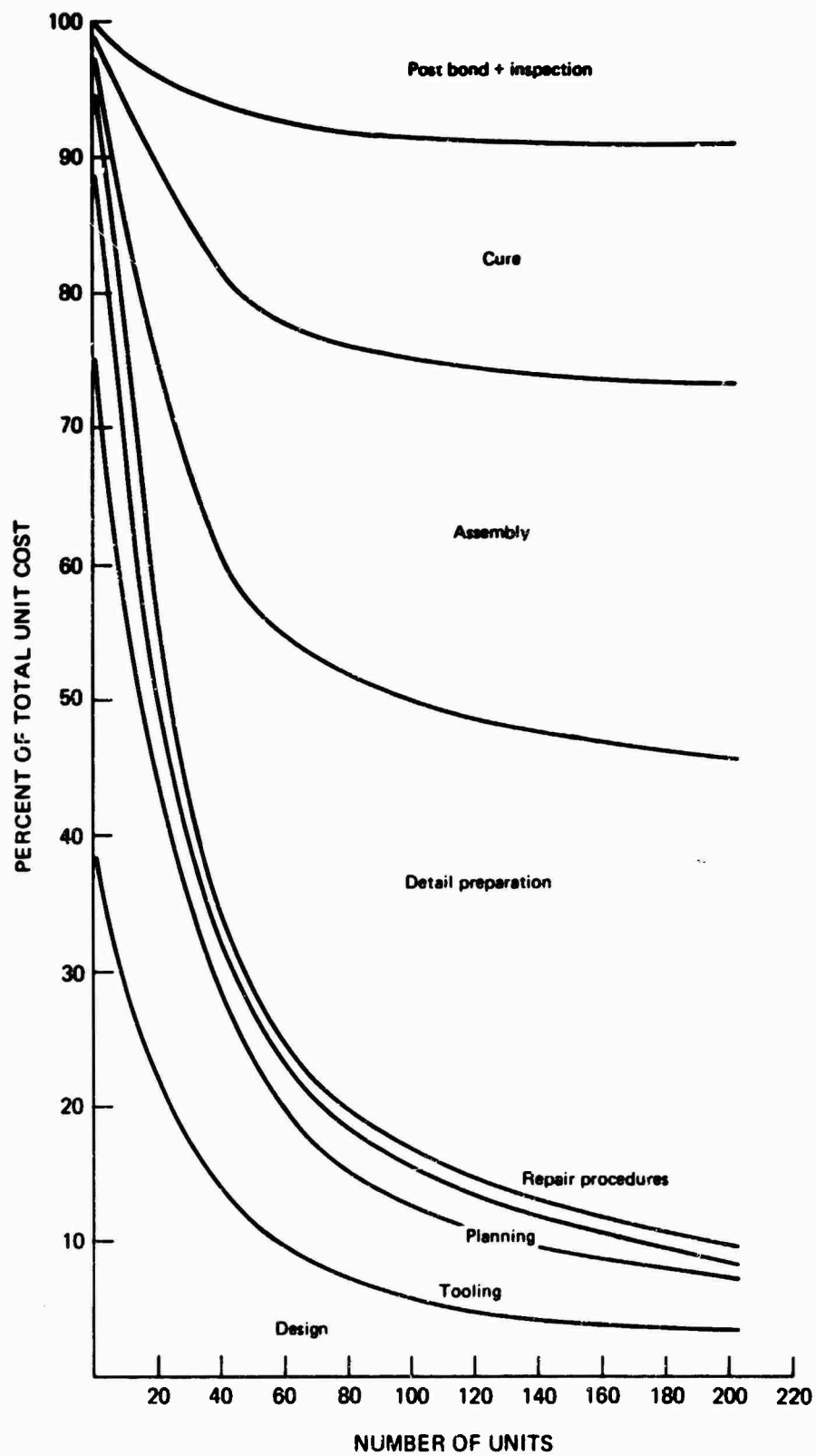


FIGURE 20  
Cost as a function of volume.

oriented programs are reduced cost and enhanced quality. A third less tangible benefit is an increase in overall understanding of adhesive bonding without any direct or obvious association with cost or performance. This latter case is more likely to result from study programs more fundamental than those normally associated with processing. In many instances cost and performance factors are inter-related, and frequently performance advantages manifest themselves in terms of cost benefits. For example, a uniformly stronger adhesive system may open the way to reduced structural weight, thus producing a more efficient (in terms of function per unit weight) bonded component in a system that can perform its mission with greater reliability. Fewer operational losses will occur, and therefore, fewer numbers of the system will be required. Yet greater life safety and mission success will be achieved.

#### 6.6.3 Adhesive Bonding Industry Scope

Any estimate of benefits obviously must start with a definition of the total size of the aerospace adhesive bonding industry. Since this industry is not really large, or well defined, there are no official records of its size. However, a reasonable current estimate is that about \$400,000,000 worth of bonded parts are produced annually. In addition, maintenance and repair costs<sup>A</sup> probably are in the order of \$10,000,000 per year. This figure, of course, is not the whole cost since loss of the use of the vehicle during repair will be a much greater cost. Countering this factor, however, is the fact that some repairs can be carried out when the vehicle is out of service for routine overhaul. Because of all these factors, it is difficult to fix a very precise dollar level on the adhesive bonding in the aerospace industry. It seems reasonable, however, to assume a level of about \$500,000,000 annually as the cost of manufacturing and maintaining bonded structures in military and commercial aircraft.

The other aspect of adhesive bonding is the value of the enhanced structural efficiency resulting from its use. As previously pointed out, a lighter, more maneuverable fighter plane is a military advantage partly measured in economics. However, its advantages go farther than that, and intangibles asso-

ciated with moral and political values are impossible to assess in a quantitative way. Perhaps it is impossible to be more specific than to state that future U.S. military and commercial aircraft, if designed without the benefit of improved adhesive bonding technology, would be at a significant disadvantage, as compared to systems using adhesive bonding developed elsewhere. It then follows that continuation of an active advanced adhesive bonding technology program is of significant, although probably not critical, importance to the future of the U.S. aerospace posture.

#### 6.6.4 Estimated Benefits Resulting from Recommended Programs

Each of the recommended programs has its own payoff spectrum and, hence, must be considered separately. Comments on each of the three major payoff areas--initial cost, maintainability, and enhanced performance--are recorded in Figure 21.

#### 6.7 Conclusions and Recommendations

This section summarizes the chapter and presents a program designed to solve the various problems that have been identified. The conclusions are presented in decreasing order of importance. It should be recognized that this list is concerned with manufacturing problems; hence, it does not cover or assigns a relatively low priority to items that may deserve more attention from the standpoint of other subject matter dealt with in the other chapters.

##### 6.7.1 Availability of Technical Data

###### Conclusion:

The most significant problem area hindering the effective use of structural adhesives is the lack of a readily available, adequate, and current source of reliable data that can be used by the designer, the materials engineer, or the manufacturing engineer. Because of the disorganized condition of the literature of adhesive bonding, and the fact that many valuable empirical experiences are never published, much useful information and many new discoveries are not available to the persons responsible for the effective use of adhesives in critical aerospace applications.

FIGURE 21 Estimated Benefits Resulting from Recommended Programs.

Degree of Impact on				
	Manufacturing Costs	Maintainability Costs	Performance	
1	Handbook, Inst. Team, Tech. Meets, etc.	Major - could reduce by 5 - 10%.	Major - could reduce by 20 - 30%.	Moderate, but in some cases might decrease slightly.
2	Repair Adhesive	Minor - might reduce in some special areas.	Major - could reduce by 10 - 20%.	Significant, in that new applications for bonding would result.
3	Detail Process Controls	Moderate - would reduce reject rate.	Moderate - through reduction of borderline quality parts.	Moderate - due to decreased data scatter.
4	Composite Machining	Significant for composite hardware.	Slight - decreased flaws should give improved service life.	Slight - reduced flaws.
5	Bulk Adhesives	Significant - could reduce 1 - 2%.	Little to none.	Minor - may increase strength or reduce weight in sandwich bonds.
6	Node Bond Adhesive	Significant reduction in core costs.	None.	Moderate - through increased use of high strength core.
7	Weldbonding	Significant - could reduce cure time.	Possible increase.	Moderate - increased fatigue life over welded parts.
8	Stage Forming of Composites	Significant for some composite parts.	None.	None.

FIGURE 21 (cont'd.)

Degree of Impact on				
	Manufacturing Costs	Maintainability Costs	Performance	
9	Low Cost NDI	Minor overall, but significant for inspection costs.	Slight.	None.
10	Uniform Specs.	Minor.	None.	None.
11	Forming Methods	Minor.	None.	Slight - through better bond line thickness control.
12	Tough HI Temp Adhesive	Significant for high temp applications.	None.	Slight - through process damage reduction.
13	Low Temp Curing Adhesive	Slight - through reduction in cure time.	Slight.	None - possible reduction in elev. temp. strength.
14	Cocuring	Significant for composite structures.	None.	None - possible slight reduction in strength.
15	Machining Damage	None.	Could be significant, depending on results.	Slight - possible reduction in data scatter.
16	Core Machining	Minor.	None.	None - may result in slight fatigue strength reduction.

FIGURE 21 (cont'd.)

Degree of Impact on _____				
		Manufacturing Costs	Maintainability Costs	Performance
17	Low Temp. Curing Adhesive	Slight - through reduction in cure time.	None.	None - possible reduction in elevated temp. strength.
18	Std. Surface Preparation	Slight - less process control facilities.	None.	None.
19	NDI for Substandard Joints	Slight - may even increase due to increased inspection costs.	Significant - through elimination of marginal quality parts.	Minor - through reduction in data scatter.

**Recommendation :**

- **Handbook of Adhesive Bonding** -- A comprehensive publication summarizing all aspects of adhesive bonding should be prepared. The book should contain design data on the various commercially available adhesives, joint design concepts, analysis techniques, tooling concepts, processing information, and projected costs to manufacture typical parts. Availability of this publication to potential users should be maximized and it should be kept up-to-date.
- **Instruction Team** -- A team of two or three experts in the various aspects of adhesive bonding should assemble and present to the various manufacturers of bonded aerospace hardware a comprehensive short course designed for designers and manufacturing engineers.
- **Technical Society Meetings** -- One or more of the technical societies should be encouraged to organize and present a series of technical symposia on the general subject of the adhesive joint design/manufacturing cost interface and to update these symposia at intervals as the progress of technology warrants.
- **Formal Education** -- Instructional material suitable for use in engineering schools should be developed and made widely available in order to advance and strengthen the coverage of adhesive bonding in formal education of future engineers and materials scientists.

**6.7.2      High Processing Costs**

One of the major deterrents to more extensive use of adhesive bonding is the relatively high cost associated with the manufacturing process. These costs are a consequence of the various elements of the manufacturing process plus the high cost of repair of parts damaged or deteriorated in service. A number of separate, but related, solutions to these manufacturing problems are to be considered.



#### **6.7.2.1 Weldbonding**

##### **Conclusion:**

The weldbonding process consists of applying adhesive in paste form to details that are subsequently assembled and spot welded. The part is then inserted into an oven in order to cure the adhesive. This process produces a high strength, fatigue resistant joint using less costly tooling than is normally required for conventional adhesive bonding. Further, this process may reduce costs through substitution of oven for autoclave.

##### **Recommendation:**

Further development of the promising weldbonding technique is recommended. The advantage and limitations of this process should be effectively established.

#### **6.7.2.2 Bulk Adhesive Application**

##### **Conclusion:**

A significant cost factor in adhesive bonding is a result of the prevailing use of film adhesives. The conversion of the adhesive into film form is costly, and its subsequent trim and hand lay-up to fit the part is even more costly. Trim material is difficult or impossible to reuse.

##### **Recommendation:**

Automated application methods for liquid and powder adhesive systems, such as hot melt coating, spray coating, powder application, etc., should be developed and used as appears advantageous.

#### **6.7.2.3 Low-Cost Nondestructive Inspection Methods to Detect Voids**

##### **Conclusion:**

The inspection of bonded panels is a costly process, frequently involving the slow scanning of the entire panel to detect the presence of voids.

##### **Recommendation:**

Rapid inspection methods whereby the entire panel can be inspected for adhesive voids in a few minutes should be developed and introduced for broad usage.

#### **6.7.2.4 Machining of Composites**

##### **Conclusion:**

The post-bond machining of bonded composites requires special tools and techniques, especially where combinations of boron/epoxy and titanium are involved.

##### **Recommendation:**

Better machining techniques for bonded composites should be developed in order to reduce machining time. These developments should aim at eliminating the requirement for expensive special tools and skills and at reducing damage to such bonded composite assemblies.

#### **6.7.2.5 Uniform Processing Specifications**

##### **Conclusion:**

The many adhesive bond processing specifications now in use for essentially the same purpose increase the cost of adhesive bonding by unnecessarily complicating the art.

##### **Recommendation:**

Standards groups (e.g., ASTM Committee D-14) should be encouraged to develop a standard for processing of adhesive bonds that could be used industry-wide.

#### **6.7.2.6 Field and Shop Repair**

##### **Conclusion:**

A significant problem area exists in field and shop repair of damaged parts since original bond fabrication conditions cannot be duplicated in the repair shop.

##### **Recommendation:**

Development of an effective adhesive system which can be cured at about 20 to 30°C to yield bond properties equivalent to the better heat-cured systems should be undertaken. Such a system would have a significant economic benefit, reduce induced thermal stresses, and facilitate many production applications.

#### **6.7.2.7 Forming Methods**

Conclusion:

The process by which the various metal details are formed prior to bonding has not been evaluated as a factor in bond strength and durability. However, low bond strength, ascribed to prior forming and treatments of the metal, has been reported. The importance of inadvertent preconditioning of the adherend needs to be defined and examined.

Recommendation:

The effect on adhesive bonding of forming lubricants, parting agents, mill or heat treat scale, and other process aids or process-oriented surface contaminants should be sought out and suitable remedies for the identified bond impairing factor should be developed.

6.7.2.8 Node Bond AdhesiveConclusion:

The cost of certain grades of aluminum alloy core material is very high due to the lack of a high peel resistant adhesive for the node bond, particularly for the stiffer, stronger alloys. A node bond adhesive with high peel resistance would make it possible to manufacture expandable core from all aluminum alloys by the low-cost HOBE process.

Recommendation:

Additional development work should be undertaken to provide effective and reliable structural adhesive systems for bonding the nodes in metal honeycomb for cores in bonded component assemblies, particularly to provide node bonds with higher peel strength so as to permit effective production of expandable metal honeycomb from stiff, high-strength aluminum alloys by the low-cost HOBE process.

6.7.2.9 CocuringConclusion:

This process aims to lower costs of composite details by applying a "B" stage composite lay-up directly to the core of a sandwich structure and curing the laminate and bond-line concurrently.

Recommendation:

Further development of the cocuring process is recommended.

6.7.2.10 Core MachiningConclusion :

The cost of machining of various honeycomb core materials to the proper tapers to fit the closeout details is an expensive process, even with the use of numerically controlled (N/C) machining methods.

Recommendation:

Alternate to core machining such as crushed core, potted resin edge closures, etc., should be developed.

6.7.3 Product Uniformity

A deterrent to the more extensive use of adhesive bonding is the inconsistent quality frequently observed in parts produced in a production environment. High scrap rates, excessive rework costs, as well as in-service failures frequently are the result of inconsistent joint quality. (Also see Forming Methods below.)

6.7.3.1 Forming MethodsConclusion:

The forming of metal details frequently introduces stresses that may interfere with proper processing or performance. For example, stress relaxation during heat curing of the bond may cause unacceptable changes in contour. Also, stresses may serve as initiation sites for stress corrosion in a humid environment.

Recommendation:

The influence of metal deformation on bonds needs to be studied.

6.7.3.2 Tough High-Temperature AdhesiveConclusion:

The brittle nature of the available high service temperature adhesive systems presents problems in further processing, especially during post-bond machining, cleanup and trim. Mechanical holding devices for riveting, if not properly configured to fully support the part, may introduce sufficient stress to

delaminate the bonded part.

Recommendation:

An adhesive system with higher peel strength than currently available would be less susceptible to this type of failure and should be developed.

6.7.3.3 Machining Damage

Conclusion:

The careless or unduly rapid machining of bonded assemblies may result in the introduction of tiny fractures at the edge of the bond line. These flaws may serve as failure initiation sites. The significance of this type of machining damage after bonding has not been adequately established.

Recommendation:

A definitive experimental program in this area is recommended.

6.7.3.4 Low Joint Strength Nondestructive Inspection Methods

Conclusion.

In spite of continued expressions of interest in a nondestructive inspection method for detecting substandard joints, there are no satisfactory methods available. Present nondestructive test methods are primarily useful to detect voids in the adhesive layer. If a reliable nondestructive procedure to detect weak joints could be developed it would contribute to the overall quality and uniformity of bonded production panels.

Recommendation:

The continued development and perfection of such test methods should be encouraged.

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## CHAPTER 7

BEHAVIOR OF POLYMERIC ADHESIVES IN JOINTS7.1 Introduction7.1.1 Purpose

In the design and evaluation of structural adhesive joints, the properties and behavior of the polymer within the joint and between the adhesive-adherend interfacial layers are always important (Figure 22). Indeed, assuming that a "proper" joint exists in which joint strength is not limited by poor interfacial bonding (see Chapter 5) (Alfrey 1967; Bickerman 1961; Huntsberger 1967; Orowan 1970), the behavior of the adhesive material in the joint must assume a critical structural role in determining performance. In general, the behavior of the material in the joint will depend on (a) the range of bulk material properties, (b) the specimen prepared method, and (c) the thickness of the adhesive layer. In actual practice, experience generally indicates that typical structural adhesive bonds between various metals fail in both laboratory tests and in service more within the adhesive film than in apparent adhesion to the adherends. This is not to indicate that adhesion and wetting of adherend surfaces by the adhesive is not a problem or that introduction of new metals and other aerospace adherends will not introduce new problems in adhesion. However, it is quite clear that from a practical standpoint improvements are needed in the bulk cohesive properties of the adhesive film in various joints and that greater knowledge is needed on the fundamental mechanisms of failure in such films and on means to minimize such failures in practice.

The purpose of this chapter is to discuss from a basic point of view, the material properties of structural polymeric adhesives within real joints and in bulk and also the process of converting a polymer or pre-polymer to the polymer in the joint. Interfacial and boundary layers (see Chapter 5) are not considered except when necessary for reasons of continuity. Technological implications are discussed in more detail in Chapters 8, 9, and 10.

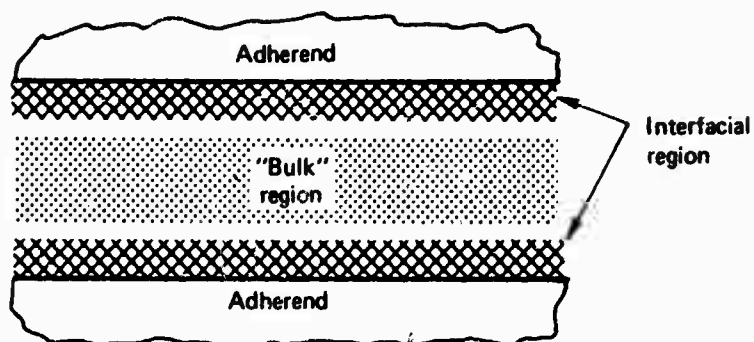


FIGURE 22 Schematic of an adhesive bond, showing both interfacial and bulk regions within the adhesive layer.



### 7.1.2 Specific Information Needs

In order to aid in materials selection, and in the prediction or control of behavior, the engineer and scientist needs certain specific information.

The joint designer needs to know:

- Stress-strain behavior over a range of temperatures, times, and environmental conditions (strength, modulus, elongation, toughness, creep, etc., both under static and dynamic loading)
- Fracture behavior, again over a similar range of conditions
- Thermal properties (coefficient of expansion, glass temperature)
- Chemical properties (water absorption, thermal and radiation stability in the presence of oxygen, fuels, other fluids, and stress); this is also known as resistance to the environment

The materials scientist and engineer needs to know relations between structure, composition, and behavior in order to recommend materials and to define processing procedures to meet performance specifications. Specific needs include:

- Type of adhesive
- Effects of joint history (curing, setting, etc.)
- How to characterize a joint, at any chosen time, by non-destructive testing
- The relationships between properties in the joint as cured and the properties of the resin in bulk or the properties of the prepolymer prior to cure

In general, detailed knowledge of relationships between joint design, material properties, and behavior are needed in themselves and as a function of test methods.

### 7.1.3 General Rationale

Behavior in a joint should resemble the behavior in the bulk (Alfrey 1969) if equivalent assumptions of identical composition, history, material parameters, specimen thickness, stress distribution, and environment can be made with assurance. In practice, unfortunately, the material parameters may be very

much affected by being in a joint; and such assumptions are generally not valid. However, it is vitally important to distinguish between effects due to the generic bulk polymer per se and effects due to variations in the parameters mentioned.

## 7.2 State of the Art

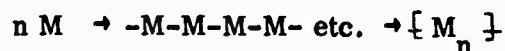
Some characteristics of high polymers are shared with other classes of materials (e.g., ceramics and metals) while some (e.g., rubber-like elasticity and time-dependence of properties) are essentially unique (Alfrey and Gurnee 1967; Billmeyer 1971; Nielson 1962). Design of any component to be used in an engineering application must reflect consideration of such fundamental differences in behavior. Further, the conversion of a raw material into a useful component involves a variety of processes, some of which are common to many materials and some unique to polymers.

The behavior of polymers within adhesive joints (e.g., the relationships between material and joint behavior) is clearly a subject of major concern. Two relationships are of interest: (a) the link between the polymer in bulk and in the unbroken or failed joint, and (b) the link between the polymer processed in the joint and the raw material (pre-polymer or polymer). Emphasis is placed on the state of development of principles that may serve to correlate otherwise unrelated and empirical knowledge, to predict behavior, and to help guide present and future research and development.

### 7.2.1 High Polymers as Materials

First, it should be useful to summarize present views of the essential characteristics of high polymers and to develop several simple principles that relate structural and compositional characteristics to characteristic material parameters such as equilibrium modulus. Behavior during preparation of a joint and during service is discussed in Section 7.2.4.

The major feature distinguishing high polymers from other materials is a very high molecular weight (from about 10,000 to practically infinity) that arises by the linking together of many small molecules of monomer into very long chains:



These long chains, which may be linear (finite molecular weight) or cross-linked to form a network (infinite molecular weight), are entangled together rather like a bowl of spaghetti (Figure 23).

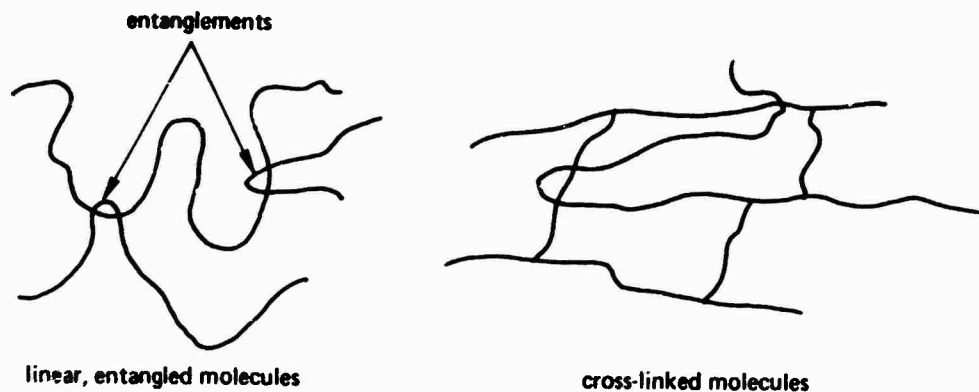


FIGURE 23 Schematic of linear and cross-linked polymer molecules.

Because of the resistance to deformation conferred by the entanglements, the mass of high-molecular-weight molecules can exhibit strength and stiffness, whereas low-molecular-weight organic compounds do not. Further, the fact that molecules may be disentangled if a stress is maintained over a period of time (as spaghetti can be with patient pulling) leads to a dependence of mechanical behavior on the time scale or rate of any measurement. Disentangling is, of course, easier the higher the temperature.

Both linear and cross-linked systems are used in adhesive applications. Since, however, cross-links represent actual chemical bonds and not just simple entanglements, they confer a greater measure of property permanence at elevated temperatures and in the presence of solvating (disentangling) media. Hence, most structural adhesives (e.g., epoxy resins) are designed as cross-linked (thermo-setting) rather than linear\* (thermoplastic) polymers. Most linear polymers are prepared by addition of one monomer molecule to another; the product of this polymerization process may then be processed by melting, as in the extrusion of a hot

\* For simplicity, branched molecules shall be included in the linear class as long as the branches are not themselves connected, a state that would constitute cross-linking.

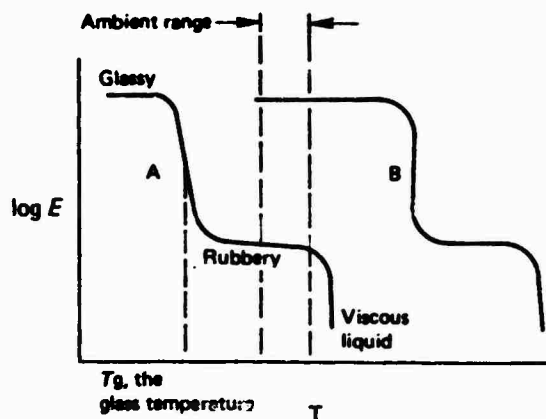
melt to form an adhesive layer. In contrast, thermosetting resins must be made by first partially polymerizing the monomer materials to give a tractable pre-polymer and then completing this polymerization in situ (e.g., actually in an adhesive joint). Thus, the chemistry of thermosetting resins is inherently more complex than that of thermoplastics; control and knowledge of a process in an actual joint is more difficult than for a process in a reactor.

Given a polymer with high molecular weight, with its implication of at least some degree of useful mechanical properties, the response to deformation must depend upon the balance between two opposing tendencies: (a) the mobility of at least segments of the long chains, and (b) the cohesion. The former tends to result in movement of the segments in response to a stress; the latter tends to restrict such response. Hence, any structural or compositional factor that enhances stiffness or sticking together will inhibit a mobile response and make it necessary to go to a higher temperature to reach a given state of response; any factor that enhances flexibility and lack of attraction between molecules will have the opposite effect.

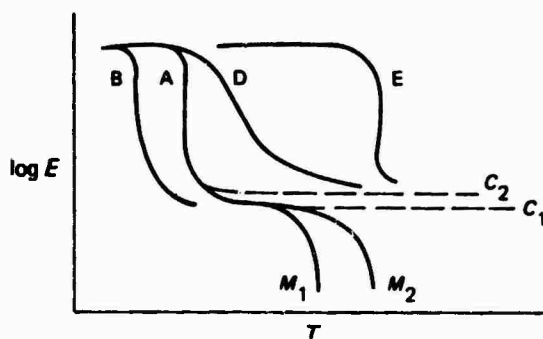
The kind of balance achieved determines whether or not a polymer exists as a plastic, or as an elastomer (rubber), at any temperature. In general, as one raises the temperature of a plastic, properties change as response becomes progressively easier. Thus, as in Figure 24, the stiffness (as measured in a small-deformation test) of a rigid plastic (in this case, amorphous) decreases greatly over a narrow temperature range (around the so-called glass-to-rubber transition), and the plastic changes to a rubbery material. The change in behavior reflects an increase in mobility and a decrease in cohesion. At still higher temperatures, stiffness will drop again for a linear polymer as viscous flow begins; a cross-linked polymer, however, will remain relatively unaffected due to the immobilizing effect of the cross-links, at least until chemical degradation occurs. Overall, the behavior changes from elastic to viscous, with a "viscoelastic" region in between.

The position of this basic curve with respect to ambient temperature determines whether or not a polymer is a plastic or an elastomer. The curves

## (a) States of Matter in Polymers



A, an elastomer at ambient temperature; B, a plastic at ambient temperature.



## (b) Effects of Composition, Structure, Morphology, and Molecular Weight

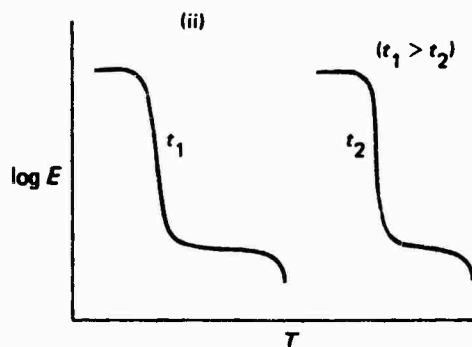
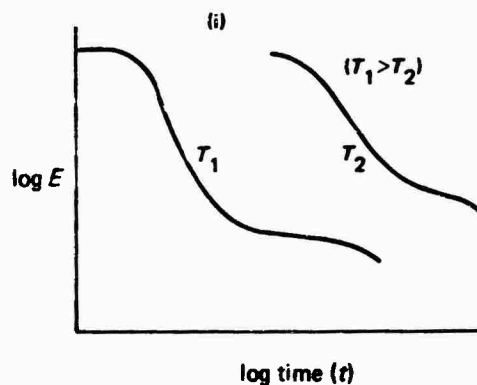
$M, M_2 > M_1$

B, Copolymer of A with lower-softening polymer;

C, effect of cross linking ( $C_2$  cross-link density  $>$   $C_1$  cross-link density);

D, blend of A with E, or a semicrystalline polymer by itself.

## (c) Time-Temperature Effects



## (c) Direction of Changes

due to Structural Factors

(i) increased cohesion  $\rightarrow$

(ii) increased mobility  $\leftarrow$

(iii) increased cross linking  $\rightarrow$

(iv) increased crystallinity  $\rightarrow$

(arrows represent direction of shift of  $E$ - $T$  curves)

FIGURE 24 Effects of structural and compositional factors on Young's modulus ( $E$ ) of a polymer, as a function of temperature and time.

will be shifted to the right or left for a given polymer depending on the mobility-cohesion balance. Factors such as polarity and linearity tend to increase cohesion and packing and shift the curve towards higher temperatures. A similar effect is caused, for a given polymer, by increasing the rate of testing; the faster the rate, the more difficult the response. Cross-linking tends to shift the curve upwards, especially in the rubbery region, and to the right in proportion to the density of cross-links. Random copolymerization of two monomers will yield a curve intermediate between those of the two components.

These effects operate in a similar fashion if stiffness (or other property) is measured as a function of time. Thus, at a given temperature, the time required to relax will be increased by the factors, such as polarity, which increase the difficulty of response, and so forth. Indeed, time and temperature are complementary variables; the greater the overall resistance to deformation, the higher the temperature or the longer the time required to reach a given state of flow. These two variables are linked mathematically to yield a "time-temperature equivalency" principle (see Chapter 9, Tobolsky 1960; Williams et al. 1955). This principle is frequently useful for correlating data on simple polymeric systems.

Other structural and compositional effects may change both the position and the shape of a response curve. For example, crystallinity not only increases stiffness but also spreads out the glass-to-rubber transition region. Block and graft copolymerization, as well as physical blending, also tend to spread out the transition region. High modulus fillers tend to raise stiffness, although not necessarily strength.

While the failure of an adhesive in a joint clearly involves much larger deformations (e.g., yielding and flow) than is implied in the above discussion, there are, at least in principle, relationships between, for example, Young's modulus and failure behavior (Section 7.2.3).

Since the material properties of concern depend very much on the processing used for any given resin or formulation (e.g., on the curing conditions

used with an epoxy resin), it is necessary to define just what the resin is as made under a given set of conditions. A given epoxy resin formulation may exhibit widely different properties, depending on the curing process, in large part because of differences in the density of cross-links (Section 7.2.4). Thermoplastic polymers also may show differences in behavior as a function of processing; (e.g., crystallinity and morphology are very sensitive to thermal and mechanical history).

In summary, the roles played by many basic material parameters are reasonably well understood, at least qualitatively. It must be remembered, however, that successful extrapolation of bulk properties to an adhesive joint will require that the material in the joint be characterizable and that real adhesive compositions are frequently complex multi-component systems.

The question of large-deformation properties, such as failure per se, is discussed in the following section.

#### 7.2.2 Large Deformations in Processing and Service

In processing and later in service polymers often experience strains that far exceed those prescribed by the assumptions implicit in the laws of linear viscoelasticity. For example, processing often involves manipulation of a polymer in the melt. This obviously involves extensive flow; large stresses in a solid may result in yielding beyond an elastic limit, considerable flow, and eventually fracture occurs. While viscous flow often can be treated, at least to a good approximation, by existing theoretically based relationships, ultimate properties such as tensile strength, impact strength, or yielding are characteristically difficult or impossible to treat rigorously. In addition, although the application of a continuum approach may serve to describe and correlate experimental data (a useful operation in itself), the real phenomena are characterized by gross inhomogeneous behavior such as cavitation, adiabatic heating, changes in the state of order, etc. Nevertheless, frequently the molecular factors operative in determining linear response and parameters such as the various moduli (elasticity, rupture, etc.) are similarly operative in the case of non-linear responses.

Typical viscous flow, often non-Newtonian at shear-rates typical of

melt processing conditions, does show a strong dependence on molecular parameters such as molecular weight and the distribution of molecular weight (Billmeyer 1971; Deanin 1972). Thus, the melt viscosity normally depends on the 3.4th power of the molecular weight -- a fact that mitigates against the general desire to keep molecular weights high in order to maximize typical mechanical properties. Since the flow of an adhesive into capillaries (Van Oene 1972) and the coalescence of polymers (Steiner et al. 1970) vary inversely with the ratio of melt viscosity to surface tension,  $\eta/\gamma$ , a similar conflict applies in adhesive behavior. It should be noted that, while the measurement of  $\eta$  as a function of temperature is a well-established technique, values of  $\gamma$  at high temperatures have been reported for only a few systems (Roe 1968). However, techniques for measuring the ratio  $\eta/\gamma$  itself recently have been successfully demonstrated (Van Oene 1972).

Effects of large deformations in the solid state are much more complex and less well understood. In tension, several characteristic types of behavior may be observed. These range (Figure 25) from brittle-elastic through viscoelastic, to rubbery-elastic--- all found in one type of adhesive or another. With typical

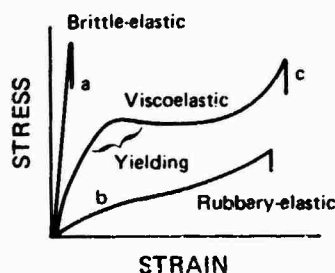


FIGURE 25 Typical types of stress-strain behavior for polymers.

glassy polymers (Figure 25a) such as an epoxy resin, the stress-strain curve is steep (high modulus) and linear until the breaking stress is reached, usually at an elongation of only a few percent. The energy to break is relatively low, even though the ultimate tensile strength is often high, and the behavior may be considered as typically brittle. With a typical cured rubber (Figure 25b), on the



other hand, moduli are substantially lower, although the presence of a suitable filler raises the modulus and ultimate tensile strength (serving to "reinforce" the rubber). Between these two extremes a diverse array of behavior is evident. With many plastics the stress-strain curves become non-linear (non-Hookean) after an initial linear portion; the stress diminishes relative to the strain, and the specimen yields in an eventually irreversible manner. From there on, the stress usually rises slowly, not at all, or even diminishes, over a range of elongation; a neck often is observed. Eventually, one of two things happens; the flowing material becomes weak to the point of breaking, or the molecules within it become sufficiently aligned (as in Figure 25c) to strengthen the mass and cause a final rise in the stress until, again, the stress required to break bonds in the now aligned and fiber-like section is reached. With stress-strain curves of this type, very large energies to break may be observed; such curves often are found with crystalline polymers, such as polyethylene, presumably because of their ability to permit deformation of the crystallites followed by re-formation during the alignment stage.

The question of ductility and toughness is of great fundamental and practical importance. While the phenomena of yielding are not fully understood, several points have become clear within the last few years, and possible mechanisms have been proposed and critically discussed (Ward 1971). In addition to shear-induced flow, one factor that now appears to be unquestionably involved in many cases is cavitation, which occurs in response to the dilational effect of an applied tensile stress. In addition to cavitation, extensive drawing of the polymer may take place, with partial coalescence of the voids to form what is called a "craze" (Figure 26) (Gent 1970; Kambour and Robertson 1972; Rabinowitz and Beardmore 1972). The effect of crazing on further behavior, is complex; it provides a mechanism for stress relaxation and the dissipation of energy but may itself constitute a weak pathway for failure. Failure by propagation of cracks usually occurs through crazed and not through uncrazed material. Otherwise general ductile yielding takes place. Which of these two

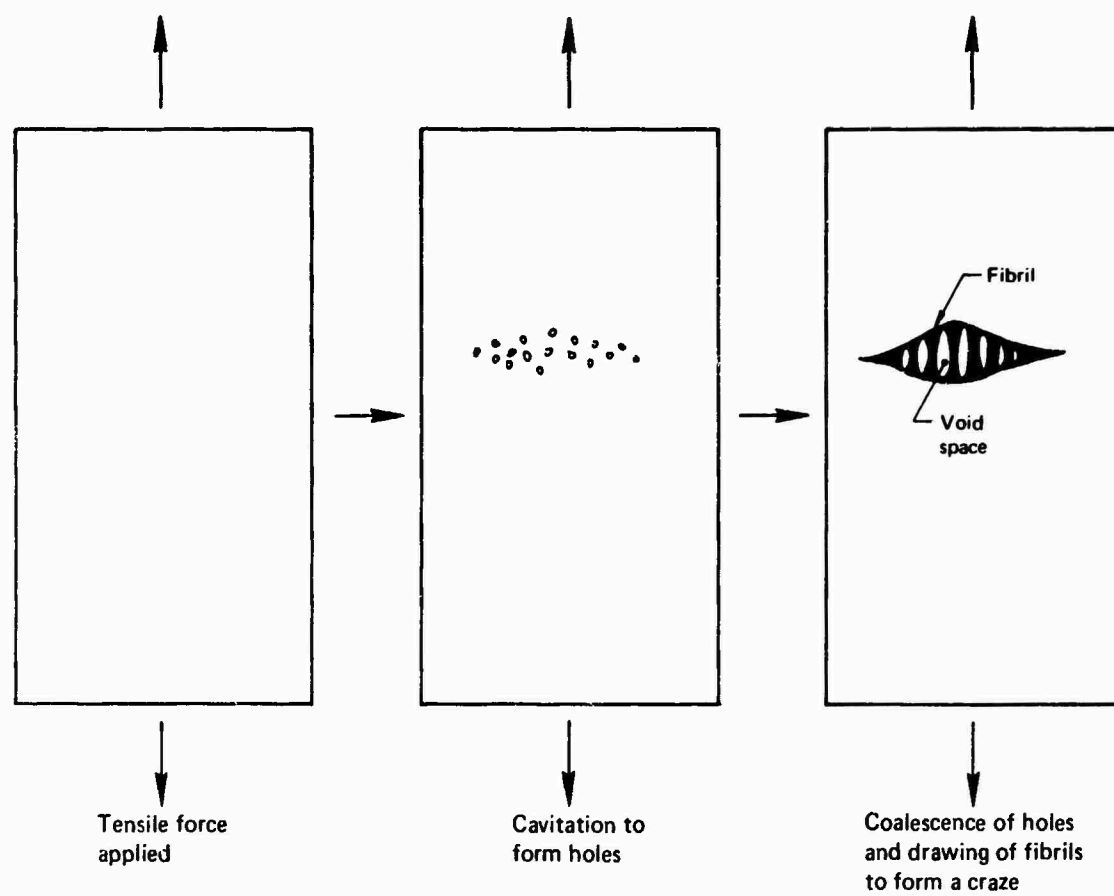


FIGURE 26 Schematic diagram of crazing induced by applying tensile force to a polymer. Crazes form at right angles to the direction of stress.

modes of failure is found to occur depends upon the stress field acting locally, the presence or absence of craze-promoting liquids or vapors, and the intrinsic properties of the polymer (Kambour 1972).

Within the past few years, better understanding of crazing has led to much greater insight into the ways in which the addition of a second rubbery phase to a brittle, glassy plastic improves toughness. The shape of the stress-strain curve (Figure 27) is changed from that characteristic of a brittle resin to one that exhibits yielding and often an extensive drawing region. Extensive craze bands appear in the glassy matrix surrounding the rubber particles (Bucknall et al. 1972; Kambour 1972; Matsuo 1969); the rubber particles evidently serve to induce a dilational stress field in the matrix. Toughening of a matrix by

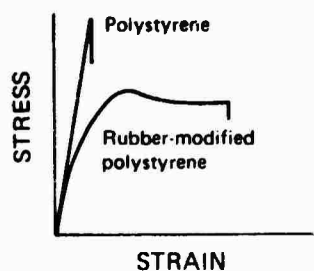


FIGURE 27 Stress-strain behavior of polystyrene and rubber-modified (high-impact) polystyrene.

introducing a finely interpenetrating rubbery polymer phase (inter-penetrating networks) also has been demonstrated (Curtius et al. 1972). Toughening is receiving a great deal of theoretical and experimental attention; such factors as phase separation, compatibility, and the effects on viscoelastic behavior, morphology, and ductility behavior are under intensive study and should be highly relevant to the behavior of many structural adhesives. By suitable control of the phase characteristics, it is becoming increasingly possible to obtain toughness without excessive sacrifice of overall modulus and to design polymer blends and related

systems to have desired combinations of properties. It should be noted that, even if crazing is not induced, dispersed rubber particles may serve to toughen a matrix by other means, for example, by stopping cracks.

The role of other components such as particulate or fibrous fillers also is receiving considerable attention. In general, fillers raise the moduli, predictable by a number of equations, depending on the relative moduli of two components and on the degree of filler-matrix adhesion. On the other hand, tensile strength and toughness are sometimes enhanced and sometimes reduced by fillers (Broutman and Sahu 1971; Di Benedetto and Wambach 1972; Fallick et al. 1966; Kumins 1965; Lange and Radford 1971; Nielsen 1967; Trachte and DiBenedetto 1971). Other properties are affected also, such as thermal coefficient of expansion, thermal and electrical conductivity, shrinkage during drying, and swelling by imbibition. For example, fillers have been shown to decrease the permeation rates of water in an epoxy resin to a significantly greater extent than predicted, presumably due to an ordering of layers of matrix adjacent to the particles (Chiu and Manson, 1973; Kumins 1965).

Of course, fracture in polymer systems, as in structural adhesives, is the ultimate phenomenon of interest in many cases (although permanent creep deformation may represent failure as well). One of the most striking developments over the past few years has been the application of fracture mechanics (Andrews 1968; Griffith 1920; Irwin 1958) to the study of not only rubbery materials... first done quite a few years ago... Rivlin and Thomas 1953... but also highly visco-elastic polymers (Irwin 1967), both in bulk and in joints (Irwin 1967; Knauss 1970; Rosen 1964). Both theoretical and experimental work is proceeding at an accelerating pace as many mechanical and metallurgical engineers turn their attention towards polymers.

Two basic approaches (essentially equivalent) have been used with variations. With one approach, due originally to Griffith (1920), the energy required to propagate a flaw of a given size is considered. The flaw may be a crack or any adventitious heterogeneity that can serve as a concentrator of stress.

The condition for growth of a crack having a length  $2a$  is given by:

$$\frac{\partial}{\partial a} \left\{ \frac{-\pi \sigma_o^2 a^2}{E} + 4aS \right\} > 0, \quad (1)$$

where  $E$  is the elastic modulus,  $S$  is the surface energy of the two freshly created interfaces, and  $\sigma_o$  is the uniaxial stress applied perpendicular to the crack. In other words, a crack of length  $2a$  will propagate if the rate of release of the stored energy  $\xi$  (equation 2) per unit growth of the crack exceeds the rate of change of the surface energy ( $4aS$ ) required by the new interfaces.

$$\xi = \frac{\pi \sigma_c^2}{E} a^2 \quad (2)$$

The critical energy for crack extension is often written as  $G_c$ , or  $G_{Ic}$  for the type I mode of crack opening (see Figure 28). Irwin has developed an alternate formulation of the problem in terms of stress. In Irwin's terms, the critical condition becomes (for the case of plane strain):

$$K_{Ic} = \sqrt{2\pi r} \sigma_y, \quad (3)$$

where  $r$  is a measure of the plastic zone at the crack tip and  $\sigma_y$  is the yield stress. It can be shown that:

$$G_{Ic} = K_{Ic}^2 \frac{(1-\nu^2)}{E} \text{ (plane strain),} \quad (a)$$

and:

$$G_{Ic} = K_{Ic}^2 / E \text{ (plane stress),} \quad (b) \quad (4)$$

where  $\nu$  is Poisson's ratio. Thus, the energy and stress criteria are essentially equivalent. The difference is in the ease of application to particular cases; one may be more tractable than the other.

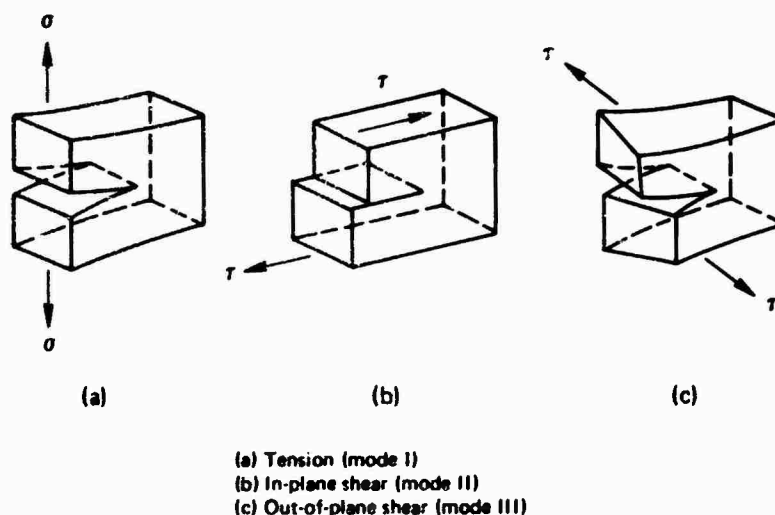


FIGURE 28 Fracture modes under which a crack can extend.

Variations also have been useful. The energy of fracture,  $G$ , is invariably found to be much higher than predicted due to plastic flow. Rivlin and Thomas (1955) have, therefore, generalized the Griffith equation to account for such processes, and Andrews and Walker (1971) have used a related modification for fatigue studies in polyethylene. Modifications to account for stress-environment interactions also have been made (see Section 7.2.3, Marshall et al. 1970). Although there is an obvious difficulty in trying to quantitatively apply continuum-type analyses to systems such as polymers in which deformation is clearly significantly inelastic and inhomogeneous, the linear mechanics do serve to characterize empirical behavior surprisingly well.

Several effects of polymer variables seem to be well established. For example, cross-linking lowers the fracture energy, presumably by restricting segmental motion (Broutman and McGarry 1965). Effects of temperature,

on the other hand, are not simple (Key et al. 1968);  $G$  may decrease and then increase as  $T$  is increased and may or may not correlate with other properties such as impact strength or yielding.

Fatigue behavior of polymers also is being studied intensively. Crack growth behavior at low frequencies can often be characterized empirically by a power-law of the form (Arad et al. 1971; Gent et al. 1964; Hertzberg et al. 1970; Manson and Hertzberg 1973; Watts and Burns 1967),

$$\frac{da}{dn} = A(\Delta K)^m, \quad (5)$$

where  $da/dn$  is the rate of crack growth per cycle,  $A$  and  $m$  are empirical constants, and  $\Delta K$  is the range of the stress intensity factor  $K$ , which characterizes the stress at the tip of the crack. \* Variations exist, for example, to account for effects of mean stress (Arad et al. 1971). At higher frequencies, adiabatic heating also may occur and cause failure by melting in polymers having high mechanical loss factors. It may be noted that the characterization of fatigue failure by the energy or stress-intensity-factor approach has advantages with respect to the conventional S-N curves (number of cycles to failure at a given stress), that is, independence from specimen geometry and a fundamental interpretation.

Effects of mean-stress, frequency, environment, and temperature have been noted, but not thoroughly explored (Manson and Hertzberg 1973). Striking differences in the behavior of different polymer structures have been observed and correlated to some extent with segmental mobility and the deformability of crystallites (Hertzberg et al. 1970; Manson and Hertzberg 1973). In general, crystalline polymers seem most fatigue resistant, at least at low frequencies; rubber-modified plastics are in an intermediate range; and glassy polymers appear poorest. Some correlations exist between  $\Delta K$ ,  $G$ , and impact strength. For example, cross-linking shifts behavior (in terms of equation 5) in the direction of increased brittleness, as it does in the case of surface energy. The use of electron and scanning microscopy should aid in relating the molecular

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\*In the equivalent energy formulation,  $\Delta K$  is replaced by a fracture energy term.

aspects to the continuum description.

In any case, it seems likely that there is now enough information at least to begin to design against failure, not only on the basis of cycles to failure plots (Arad et al. 1972; Gent et al. 1964), but also on the basis of crack growth, as has been done successfully for metals for some time. However, much remains to be done with respect to testing (and improving if necessary) existing theories, especially with complex polymer systems, and the various configurations of joints (see Chapter 8).

### 7.2.3 Mechanics of Failure in Adhesive Joint

#### 7.2.3.1 Types of Loading

Three fundamentally different modes of stressing an adhesive joint to bring about failure may be distinguished (Figure 29) as shear (lap shear), tension and cleavage (peeling). The first two correspond to forces acting on relatively rigid adherends and directed respectively parallel and perpendicular to the interface; the third corresponds to an applied tensile load, the effects of which are transmitted to the interface by a relatively flexible adherend.

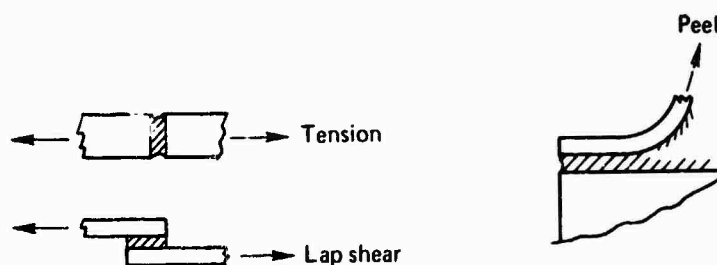


FIGURE 29 Schematic diagram of tension, lap shear, and peel tests.

By making use of the concepts described in Section 7.2.2, an energy criterion for failure, either of the adhesive itself (cohesive failure) or of the interfacial bond (adhesive failure), may be applied to each of these loading conditions (Chang et al. 1972; Gent 1971, Gent and Kinlock 1971; Mostovoy and Ripling 1970; Mostovoy et al. 1971; Ripling et al 1971 a and b; Williams and DeVries 1971) both in static and fatigue loading. The criterion may be extended to include joints exposed to aggressive media



such as water and should provide a useful basis for the control of fracture behavior in adhesive joints (Corten 1971). Predictions of the locus and path of failure have been made by several investigators (see for example, Brown and Luken 1961; Erdogan and Gupts 1971; Good 1972; Knauss 1971; Tratina 1972) for typical adhesive joints containing viscoelastic and elastic adhesives. Of course, S-N curves (number of cycles to failure at a given stress) are still useful; however, as mentioned above, such curves are not interpretable in terms of fundamental material and stress parameters. Thus, at least in principle, it should be possible to separate the geometry and stress distribution in a joint from the material properties (Young's modulus and fracture toughness) and to characterize or predict both the type of failure to be expected and the critical conditions. Of course, it is the nature of the resin system within the joint that counts. Further development of the "micro-property" method should be useful (Hughes and Rutherford 1968; Rutherford 1961; Shen and Rutherford 1971; Zabora et al. 1971) for the properties of a given adhesive appear to be very much influenced by being in the joint. Indeed significant and often complex effects of parameters such as thickness and the mode and rate of loading have been reported (Shen and Rutherford 1971). Presumably constraint by the adherend surface must play a major role in determining at least some of these effects and, as pointed out in Section 7.1.3, in changing values of material parameters for a polymer in a joint from values in bulk.

Depending on the type of loading, the energy criterion for failure does yield quite different answers for the applied forces at which failure will occur for two reasons: First, the deformation energies under given loads do not change in the same way as the failure zone propagates. In other words, the stress,  $\sigma_0$ , in equation (2) is not related to the applied force in the same way under these three different loading conditions. Studies of stress distributions clearly become important to complement information on the material properties of the adhesive. Indeed, rather good agreement between observed and predicted strengths of lap shear specimens has been reported (Greenwood 1966). More sophisticated

analyses show promise of calculating the stress in a joint and relating to performance (Cassidy et al. 1972; Harrison and Harrison 1972; Kutsch<sup>a</sup> and Hofer 1969; additional references are cited in Chapter 8).

Second, the failure forces depend in different ways upon the properties of the adhesive. For example, to maximize the tensile strength of a joint the adhesive layer should be made as thin and as hard as possible so that the available deformation energy for a given load is minimized (Cassidy et al. 1972; Harrison and Harrison 1972; Orowan 1970; Simpson and Soper 1970). Also voids, flaws, or regions of poor adhesion should be held to a minimum size ((a) in equation 2), to minimize local stress concentrations. On the other hand, when failure occurs by peeling away a relatively flexible adherend, the thickness and hardness of the adhesive are, in principle, unimportant. In practice, it is advantageous to make the adhesive layer thick and extensible so that energy is expended within the adhesive layer, as well as in creating new surfaces, when the fracture zone propagates (Gent and Kenlock 1971; Harrison and Harrison 1972; Kutscha and Hofer 1969; Orowan 1970). Also, in this case the presence of small flaws or poorly bonded regions is of relatively minor importance. Indeed, there are some grounds for concluding that a flawed adhesive would show superior resistance to cleavage failure.

Thus, the steps that should be taken to maximize the bond strength are quite different for different loading conditions, and it is not feasible to develop generally applicable rules. Instead, it is necessary to consider each loading condition separately, in the light of the Griffith-Irwin fracture energy criterion, in order to decide what design features or adhesive properties are required to minimize the energy available for crack propagation.

#### 7.2.3.2 Types of Failure

Apart from interfacial failure (treated in Chapter 5), the adhesive itself may fracture in a number of different ways depending upon its physical state. These modes of fracture are outlined below for the main classes of adhesive.

#### 7.2.3.2.1 Rubbery Adhesives, As In Pressure-Sensitive Tapes, etc. (Orowan 1970)

Failure may be of three kinds: smooth and sharp tearing under low forces for materials with low strength; intermittent rough tearing (so-called "knotty" tearing) under high forces for strong materials containing "reinforcing fillers, such as carbon black; and ductile flow at low rates of loading, like a stringy liquid, in the absence of any permanent intermolecular bonding.

The second mode is greatly to be preferred. It is not clear exactly what properties the adhesive must possess to exhibit this type of fracture, however. Although certain reinforcing fillers are advantageous, some rubbery solids show high tear resistance in the unfilled state, notably when they have high energy-absorbing characteristics (e.g. due to strong intermolecular associations or low temperatures).

#### 7.2.3.2.2 Glassy Adhesives, e.g., Epoxy Compounds

Provided that the molecular weight is sufficiently high, these materials fail in one of two ways: At low temperatures or high rates of loading or in the presence of certain stress-corrosive liquids and vapors, they break in a somewhat brittle manner by the formation of microscopic cavities in a thin band of material (craze) at the tip of a stress-concentrating flaw. The cavities then coalesce to form the fracture plane. At high temperatures or at low rates of loading, on the other hand, the conditions for cavitation are not achieved before gross plastic yielding occurs. This is the preferred mode of failure because it is associated with a reduction in stress concentrations so that only localized non-catastrophic failure takes place. Unfortunately, the conditions for the occurrence of plastic yielding rather than brittle fracture are not fully understood, particularly for heterogeneous glassy materials.

#### 7.2.3.2.3 Crystalline Adhesives, As Used In Some Hot-Melt Applications

These materials also can fail either in a brittle or a ductile fashion depending upon the rate of loading, the temperature, and the environment. In addition, the crystal structure affects the fracture mode; therefore the properties depend also upon the temperature of application, the rate of cooling, and the

annealing conditions employed. These fracture properties are the most complex and least understood of all; thus, only gross generalizations are possible. The requirements for yielding, rather than brittle fracture, appear to be: high molecular weight, small crystallite size (i.e., rapid cooling from the melt), and a high density of crystal structures so that the interspherulitic dimensions are small. The latter feature can be achieved both by rapid cooling and by suitable crystal seeding techniques.

In summary an increased understanding of the mechanics of failure of adhesive materials is greatly needed in order to carry out a rational analysis of adhesive joint strength and service life. However, existing predictions have been tested in only a few cases and in a limited range of environments; extension to more complex systems, such as filled systems, remains to be demonstrated. In spite of the promise offered by the combination of fracture mechanics with morphological studies (Broutman and Sahu 1971; Di Benedetto and Wambach 1972; Trachte and Di Benedetto 1971) research has been confined to relatively few laboratories. Further progress should greatly enhance the possibility of correlating the behavior of polymers within a joint with the behavior outside.

#### 7.2.4 Conversion to Polymer in the Joint

As mentioned above, the behavior of an actual polymer specimen (whether in a joint or not) depends directly upon basic material and environmental parameters such as modulus, affinity for water, the nature of heterogeneities, and the temperature, environment, and stress field experienced. Of course, chemistry (in the sense of the molecular weight, morphology, composition, degree of cross-linking, cohesive forces, etc.) is important, for it in turn determines the material parameters. In general, to obtain useful and reproducible joints one must control the following:

- a. Modulus and toughness (Poisson's ratio changing little from polymer to polymer)
- b. Coefficient of thermal expansion in order to minimize stresses in a joint
- c. Wetting
- d. Environmental sensitivity, such as swelling in water

- e. Morphology (voids, crystallites, gel particles, etc.), which often in turn controls properties such as toughness
- f. Composition, and its variation throughout the adhesive layer

Some of these factors are important in hot-melt joints, some in joints containing thermosetting resins, and some in both types of joint. Most are affected by the conditions used in processing or fabricating the joint. This section will review briefly the state of the art with respect to converting a polymer or pre-polymer to a polymeric material in a joint. Emphasis is on the conversion process itself, on essentially cohesive failure (with the exclusion of surface phenomena discussed in Chapter 5), and on typical thermosetting polymers, such as epoxy resins (for a particularly thorough and up-to-date review, see Lewis and Saxon 1973), there being few basic studies of hot melt behavior. Particular attention will be given to curing, the means of converting a pre-polymer to a functional polymer state.

#### 7.2.4.1 Control of Modulus and Related Properties

Pre-polymers may be selected to control such parameters as modulus of elasticity, stress concentrations, and toughness. Stresses can be distributed within a joint by the use of polymers which are highly viscoelastic, or by incorporating small voids (Lewis and Saxon 1973; Vincent 1967); the increased compliance permits more extensive deformation prior to failure. However, as indicated in Section 6.2.3, increased compliance and viscoelastic response is desirable in joints exposed to peel rather than to other types of loading. It seems possible to obtain both high modulus and localized viscoelastic response in bulk polymers (Manson and Hertzberg 1973) and, presumably, in adhesive layers. It may be that the high lap shear strengths reported for epoxies modified by the incorporation of nylon or polyurethane resins -- the former ductile, and the latter rubbery -- may be due in part to toughening without significantly decreasing the overall modulus. With a few exceptions (Simpson and Soper 1970) the role of epoxy additives, however, appears to have been investigated little or not at all. Viscoelastic response per se can of course be maximized by blending with

polysulfide or silicon elastomers, while rigidity can be conferred by using pre-polymer curing agent systems that contain rigid structures such as cycloaliphatic groups (Greenwood 1966). With the exception of the micro-property work (examples of which are cited in Brown and Luken 1961; Greenwood 1969; Hughes and Rutherford 1968; Rutherford 1961; Shen and Rutherford 1971; and Zabora et al. 1971), measurement of moduli within a joint does not appear to have been studied extensively.

Control of stress distribution across the joint is important also; the "principle of continuity" (Lewis and Saxon 1973) states that there should be no abrupt transition in mechanical properties on going from the interface to the interior of the joint. This principle underlies the concept of the graded seal between two dissimilar materials; it also provides a basis for one approach to the toughening of filled polymers (Fallick, et al. 1966). Certainly in hot melts, gradations in properties must occur across the polymer in the bond, as in the case in many molded specimens, due to thermal gradients and surface energy effects during both heating and cooling (Sharpe 1972). Gradations also must arise during the curing of thermosetting resins due to migration of individual components. However, the question of continuity has been virtually ignored in the study of adhesives; Lewis and Saxon (1973) cite only one such study.

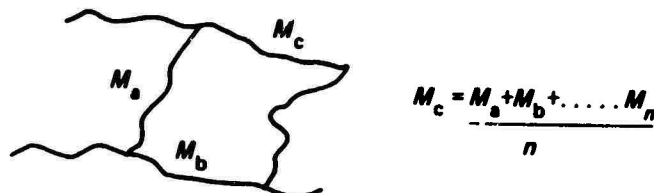
In short, in spite of a good deal of empirical knowledge of modulus and related mechanical properties surprisingly little is published about overall process of solidification or curing within a joint or about curing even outside of a joint. Because of the importance of curing, a discussion follows.

#### 7.2.4.2 Curing and Mechanical Properties

A given rheological state (i. e., a given modulus, viscosity, etc.) may be reached by changing the degree of cure (essentially, degree of cross-linking) or by changing the temperature (see Figure 24, p. 154). For a given temperature, then, the major factor is the tightness of the cross-linked network, as implied in the cross-link density. It is worth noting that the degree of cure is one of the least understood aspects of thermosetting resin technology (Lewis and

Saxon 1973).

The cross-link density is usually expressed in terms of the average molecular weight between cross-links,  $M_c$  :



Up to some point, strength and modulus are roughly proportional to the reciprocal of the average molecular weight between cross-links  $(M_c)^{-1}$  (Deanin 1972); eventually, however, the system becomes so brittle that reasonable stresses can no longer be maintained without failure. The value of  $T_g$  and the modulus in the rubbery state also vary with  $M_c$ ; unfortunately, most relationships require at least one empirical parameter (Cassidy et al. 1972).

Values of  $M_c$  for a cured resin may be estimated knowing the structure and composition of the resin components, and assuming that all, or some fraction of the reacting functional groups are reacted (see, for example, Kwei 1968 and Lin and Bell 1972). In practice, the calculation is not always easy for several reasons. First, one often can only infer the composition and details of the curing reactions. Most epoxy resins, for example, have multiple potential reaction sites; some of these may react under different conditions than others. Second, not all functional group reactions lead to true cross-links; some lead only to dangling chain ends that must be discounted as ineffective with respect to any contributions to the modulus. Since the curing takes place over an extended period of time and since at some state the mixture gels (raising the possibility of diffusion control of the curing reaction), great diversity of behavior is possible. Also, preferential adsorption of one component on a filler or at the interface, as well as phase separation in the bulk,

may occur and effectively alter the nominal stoichiometry.

Experimental verification of  $M_c$  values is, therefore, necessary, in order to find out whether or not the assumptions made in the structural estimation are correct. For this purpose, values may be estimated from the modulus in the rubbery state,  $E_r$ , by means of the equation of state for an ideal (unfilled) rubber (see Flory 1953, p. 470), which leads to:

$$E_r = \frac{d RT}{M_c}, \quad (6)$$

where  $d$  is the density,  $R$  and  $T$  are the gas constant and absolute temperature, respectively, and  $M_c$  is the average weight between cross-links. Values also may be estimated by measurements of swelling (see Solomon 1972),

$$q_m^{5/3} = \left( \frac{M_c}{d} \right) (1 - 2M_c/M) (1/2 - \chi_1)/V_1, \quad (7)$$

where  $q_m$  is the volume ratio of the swollen to the unswollen network ( $V/V_0$ ),  $M$  is the primary molecular weight (equal to infinity in a perfect network),  $\chi_1$  is a parameter characterizing the inherent polymer-solvent interaction, and  $V_1$  is the molar volume of the solvent. The term  $(1 - 2M_c/M)$  corrects for dangling ends; the use of equation (6) is clearly more direct for a complicated structure such as an epoxy resin.

Young's modulus may be determined by static or dynamic methods, e.g., a torsional pendulum (Nielsen 1962). A dynamic method, i.e., a method that gives both the storage and loss moduli ( $E'$  and  $E''$ , respectively), is often preferred.

Such methods, however, are experimentally restricted to self-supporting specimens and, thus, can give information only about adhesive resins that already have been cured to at least a minimum extent. This problem can be avoided, however, by use of the torsional-braid technique, originally developed by Lewis and Gillham (see Gillham 1973, Lewis 1963, and Lewis and Gillham 1962



and 1963). This technique involves the impregnation of a porous braid woven from glass fibers and the measurement of the damping behavior of the prepolymer-braid system. Although the method does not give an absolute value for moduli, it does give relative values and, of course, the damping peaks as a function of temperature.

The torsional-braid technique is of particular interest to the study of adhesives (and coatings as well) because it permits characterization of the rheological state of all stages during adhesive cure. Thus, it can follow the variation of modulus (or viscosity) as a function of:

- a. Curing time at a given temperature
- b. Temperature
- c. Programmed combinations of curing time and temperature (cure cycles)
- d. Solvent evaporation
- e. Degradation by thermal, oxidative, or radiation environments

When coupled with standard thermoanalytical techniques (Differential Thermal Analysis, Thermo Gravimetric Analysis, Differential Scanning Calorimetry, etc.), the braid method offers an exceptionally useful approach to basic studies with direct relevance to curing and degradation process. Of course, the other thermoanalytical techniques are necessary in order to characterize the thermal aspects of curing and degradation reactions, such as heat of polymerization and energy of activation.

Curiously, in spite of the availability of this technique for a number of years, little use has been made of it in the quantitative study of adhesives, whether for curing or degradation (Lewis and Saxon 1973). One study of curing in epoxy coatings (Lewis 1963), some preliminary studies of polyimide curing reactions (Gillham 1973), and a few more detailed studies of epoxy adhesive systems (Lewis 1967; Lewis and Elder 1968; Lewis and Ramsey 1966) have been reported. Correlation with joint strength data has been reported for only one system, an amine-cured bisphenol-A epoxy resin (Lewis 1963). Because of

its general applicability to cured adhesive systems, it is worthwhile to summarize this study.

The thermosetting curing process of an amine-cured epoxy system involves the transformation of a viscous liquid pre-polymer, first to gel and eventually to a typical glassy, rigid polymer -- the whole process being in essence a reversal of the sequence discussed in Section 7.2.1 (see Figure 30).

Two other interesting and exceedingly important points may be noted. First the rate of curing is known to decrease when rigidity is attained (see time scale of Figure 29). Second, gelation apparently occurs prior to the glass transition, as implied by the small peak A. The development of adhesive joint strength appears to parallel the glass transition curve. Indeed, in one of the few analytical approaches to the problem, the development of joint strength as a function of curing may be given in the form of a simple relation (Gillham 1973):

$$f = f_{\infty} - (f_{\infty} - f_0) \exp(-t/\tau), \quad (8)$$

where  $f_{\infty}$  is the equilibrium strength which is approached asymptotically with time,  $f_0$  is the initial strength,  $t$  is time, and  $\tau$  is a characteristic time corresponding to the time required to reach the glassy state. If  $\tau$  follows an Arrhenius relationship characterized by an activation energy,  $E$ , with respect to temperature:

$$\tau = A \exp(E/Rt), \quad (9)$$

then the rate-determining step in the cohesional setting can be approximated by a simple rate expression for the rate of the cross-linking reaction.

In any case, determination of behavior as it interacts with the energetics of curing appears to hold exceptional promise as an approach to characterization curing of adhesives but does not yet seem to have been applied to any significant degree. One exception has been the combination of differential scanning calorimetry (DSC) and thermomechanical analysis to isolate the effects of metal fillers in an adhesive on the kinetics of curing and mechanical response in epoxy phenolic and polyimide adhesives (Kaelble and Cirlin 1971).

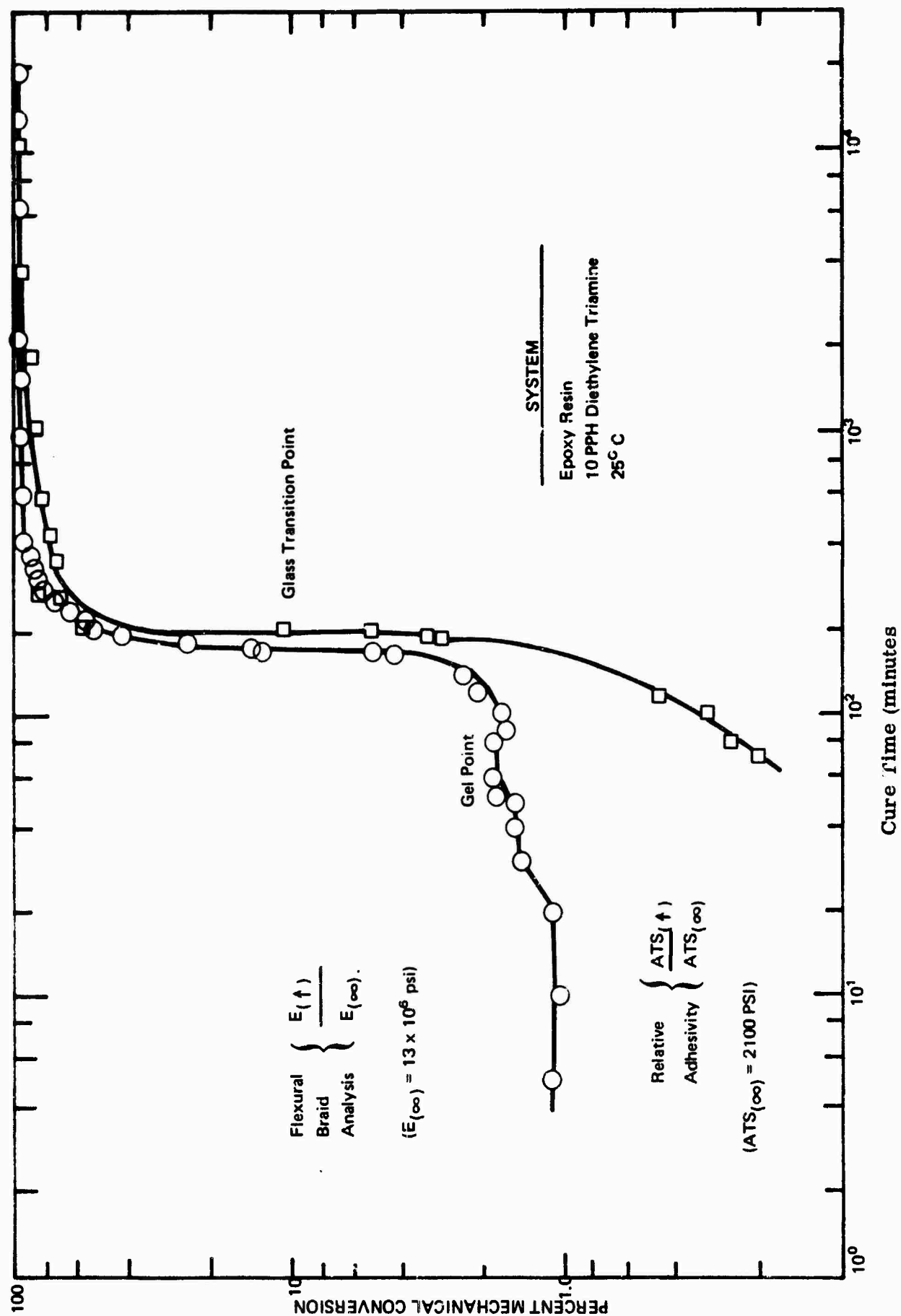


FIGURE 30 Development of Adhesive Joint Strength and Mechanical Stiffness During Curing of an Epoxy Resin.

#### 7.2.4.3 Processing in Hot Melts

It is well known that the mechanical properties of thermoplastic resins are sensitive to thermal and mechanical history. Frequently, quenching results in improved performance, presumably by yielding small crystallites tied together by disordered segments, which can serve to distribute stresses, rather than large crystallites connected by strained segments and possibly containing voids (see Section 7.2.3). In addition, orientation may occur during flow or during solidification.

As with the other topics related to processing, little has been reported with respect to the solidification process in hot melts, which appear to have been little used as structural adhesives. However, the general conclusions mentioned in the previous paragraph with respect to behavior in bulk tended to be borne out in a study by Nakao (1972), who reported that the quenching of polyethylene, nylon, and polyethylene terephthalate tended to improve adhesive bond strength.

#### 7.2.4.4 Chemical Aspects of Processing

Not only must the cross-link characteristics affect the modulus, they also must affect the permeation and equilibrium swelling behavior. In turn, the effects of an aqueous (or other) environment in changing the stress response (by plasticizing the resin and swelling it under constraint) and in inducing possible chemical changes also must be related to the degree of cross-linking as well as to the chemical affinity for water. (The latter may be changed by changing the chemical structure.) Basic engineering studies of moisture absorption as a function of network characteristics appear to have been neglected.

Similarly, the permeability and stress cracking behavior of thermoplastics -- such as may be used in hot melts -- are known to be sensitive to morphology, but the subject of hot melts seems also to be neglected.

#### 7.2.4.5 Alternate Processing Methods

Although the thermoset curing and hot-melt methods are the most common processing methods used, it is worth mentioning several other possibilities. Basically two approaches may be considered -- changing the means

of introducing energy and changing the sequence of bonding and the physical state of the adhesive.

One alternate method for introducing energy in structural adhesive bonding is the use of radio-frequency energy (RF), i. e., energy having a frequency the order of megacycles or (usually) higher. This method is used extensively for structural adhesive bonding, for the bonding of plastic to plastic, and, to an increasing extent, for bonding plastic to other materials (Farkas 1964; Marshall 1972). The method sometimes but not always lends itself to repetitive or even continuous bonding and involves heating up (in general) mainly the adhesive. The usual problems of wetting and solidification apply, and electrode configurations may pose a problem for complex shapes. \*

Variations in bonding sequence and in the physical state of the adhesive are possible and are receiving some attention. Examples include simultaneous curing and adhesive bonding of fiber-reinforced composites and the use of filamentary adhesives, which, on curing, preserve their orientation and presumably the benefits thereby derived (Elliott 1972). Another interesting example would

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\*As a matter of history, radio-frequency (high frequency) curing of thermosetting resin adhesives is a well-established practice in wood gluing, primarily with urea-formaldehyde resin adhesives. This goes back to World War II days and is currently in routine use in the furniture industry and in some other wood gluing operations. The principal interest is in heating the glue line without need to heat the wood adherends and, thus, to achieve rapid curing without having to drive conventional heat through masses of wood, which have low thermal conductivity. The process has been developed empirically and never studied from a fundamental standpoint. Typical commercial applications have been in edge-gluing lumber and in laminating heavy timbers; with the latter, the practical problems of providing the necessary electrodes within the heavy clamping for pressure provide problems except for repetitive production of stock sizes of straight beams, for which there is still a limited market. It is also used (high frequency curing) for various assembly-type gluing applications as in assembly of chairs. These are all a type of structural adhesive application, and were used to some extent during WW II for fabrication of wood aircraft. This is noted only as background to indicate that high frequency curing of thermosetting resins is no longer in its infancy -- R. F. B.

consist of sintering techniques. An advantage of sintering is that relatively little energy is needed, since predominantly surface flow is involved. Indeed, this technique is the key to powder-coating technology, which is now well advanced. A disadvantage is the difficulty of achieving a good balance between curing of an epoxy resin on the one hand, and flow on the other.

In summary, the quantitative characterization of typical adhesives as materials in a joint (or, for that matter, in bulk) and for the relationship to processing conditions and service behavior appears to be in a relatively early stage of development.

### 7.3 Problem Areas

A profound gap often exists between theoretical understanding of polymeric systems and their application in engineering components. The same is true for structural adhesives. Knowledge and experience of both kinds -- theoretical and empirical -- must be integrated to produce a coherent adhesion technology. Unfortunately, no professional organization exists that would bring together adhesion specialists of every kind; as a result, the diverse groups in the field appear to remain rather insulated from, and often unaware of, one another.

Quantitative information about the fracture properties of adhesives is sadly lacking. Although much attention currently is being given to yielding and drawing processes and to fracture of homogeneous polymers in bulk, data on the effects of the most obvious design parameters such as surface finish, time under load, and environmental conditions (temperature, humidity, oxygen pressure, etc.) as applicable to adhesives in joints are often not available. Also, the exact stress conditions under which the sample is broken is often not well defined, i. e., the stress distribution in the specimen and, in particular, the magnitude of the dilatant stress component, is not known. These limitations make it difficult to compare experimental observations with theoretical predictions in a meaningful way. Finally, information about the fatigue properties of adhesives under repeated loading, especially in the presence of aggressive environments, is grossly inadequate for design purposes.

Understanding of the strength of heterogeneous polymer systems (e.g., polymer composites) is also at a relatively early stage. More information is required on the effects upon the fracture properties of the composite of the size of the dispersed-phase droplets, their composition and physical properties, and their interaction with the matrix. This is particularly relevant to adhesives, which often contain a second phase. (For example, epoxy resins may be heterogeneous on a micro scale due to the kinetics of curing reactions in glass-forming substances.)

Understanding of the effects of chemical, thermal, and mechanical conditions imposed during the formulation of adhesive bonds upon their strength also needs further development, both for homogeneous and heterogeneous systems. More knowledge is needed about: (a) the curing of thermosetting polymers as a function of cure conditions (temperature, pressure, etc.) and the relationship between these conditions and the properties of the final resin system in joints; and (b) the effects of processing conditions on the morphology and properties of hot-melt resins, particularly as applied in structural joints.

The relationship between bulk properties of an adhesive and its behavior in joints has received relatively little attention. While it is well known that size and surface imperfection effects affect the cohesive strength of solids, little attention appears to have been paid to the question of whether the adhesive as a thin layer between necessarily imperfect surfaces is different in strength from the bulk material.

The relationship between joint strength and mode of loading is inadequately understood. Predictions based on stress analysis are incomplete and experimental studies have received less attention than might have been expected. In some cases a limiting strength, predictable by examining the resin in bulk, appears to govern fracture of the joint, but information is not available in many important cases.

It is clear that relatively few long-range research programs have been carried out dealing with relationships between the basic chemical and physical properties of adhesives, the loading conditions to which the joint is subjected, and

the resultant joint strength. Scientific and engineering literature on the subject, apart from inaccessible project reports with specific and rather limited aims, is quite sparse.

#### **7.4 Conclusions, Recommendations, and Benefits**

##### **7.4.1 Conclusions and Recommendations**

Several conclusions and corresponding recommendations that embrace the state of the art, current problems, and possible solutions may be stated. Although it is difficult to assign precise priorities and expected benefits from basic, long-range research programs, in contrast to technological developments, estimates are given of priorities and benefits for the various recommended actions, with the recognition that they should be subject to revision and understanding advances. It also should be noted that the various individual conclusions and recommendations are not independent; they should be viewed as a whole rather than in parts.

##### **7.4.1.1 Material Properties as a Function of Service Behavior**

Conclusion: Quite apart from fundamental research, insufficient information is currently available on existing structural adhesive systems to allow the joint designer to predict stiffness, strength, and anticipated service life of the bonded assembly with various adherends and joint configurations.

Recommendation: Programs should be developed to provide basic material properties of selected structural adhesives, such as Young's modulus, yield stress, tensile strength, fracture energies, extensibility, thermal properties and chemical reactivity, as functions of temperature, time, and anticipated service conditions for the bonded joints.

Priority: High

##### **7.4.1.2 Properties of Adhesives During Cure in Joints**

Conclusion: Serious gaps exist in our knowledge of rheological, chemical, and morphological properties of adhesive films during the manufacture of joints, and their effect on ultimate joint performance. Specifically, more needs to be known about the effects of changes in the adhesive film during curing of thermosetting



resins and the solidification of melts in joints on final joint performance.

Recommendation: Research programs should be initiated to characterize the effects of typical adhesive bonding techniques on resultant rheological, chemical, and morphological properties of adhesives in the form of thin films under pressure, as in joints, using appropriate thermoanalytical techniques (e.g., torsional-braid methods, differential thermal analysis, and thermogravimetric analysis).

Priority: High

#### 7.4.1.3 Adhesive Failure Modes as a Function of System Structure

Conclusion: Understanding of the relationship between the structure of two-phase bulk polymeric systems and their resultant viscoelastic and fracture behavior under various loads and service conditions is improving rapidly but still must be applied more extensively to structural adhesives in joints.

Recommendation: Research should be initiated on the modes of deformation and fracture of composite adhesives in various joint configurations and under various types of applied loads, as functions of polymer structure and composition, joint design, loading conditions, and service environment. Special attention should be given to the potential benefits of fillers and rubbery inclusions in strengthening such polymeric structural adhesives.

Priority: High

#### 7.4.1.4 Bulk Properties Versus Thin Film Behavior

Conclusion: Due to surface energy and stress concentration effects, the behavior of a polymer in a joint is likely to be strongly affected by the physical and chemical nature of the adherend surface and the adherend surface contour. Better understanding is needed of the relationship between bulk properties and behavior in a joint.

Recommendation: A long-range, unified research program should be initiated to correlate performance of a polymeric adhesive composition in bulk and in the joint. This program should involve stress analysis and fracture mechanics (given specific attention below) and consider mechanisms of setting, curing and hardening, effects of morphology and composition of the adhesive and surface-induced phase separations for

both well-established and novel structural adhesive systems.

Priority: High

#### 7.4.1.5 Analysis of Actual Design Configuration

Conclusion: While considerable progress has been made in the analysis of stress distributions in certain model joint configurations, including the effect of small unbonded areas, technical information is incomplete with respect to practical joints under complex load and deformation conditions of interest to the aerospace industry.

Recommendation: Research programs should be directed towards theoretical analysis of stress in various joint configurations, including the effects of layered adhesives, flaws, and unbonded areas, rough interfaces, deformable adherends, and elastic-plastic behavior of the adhesive and/or adherend.

Priority: High

#### 7.4.1.6 Evaluation of Fracture Phenomena

Conclusion: One principal problem in adhesive bond performance is the lack of understanding of the conditions under which fracture will occur, either during void formation or in subsequent loading and service. The understanding is important for relating simple quality control tests of joints to service, for predicting the useful life of adhesive joints, and for the design of improved bonded joints.

Recommendation: Standard experimental techniques for evaluating the fracture phenomena of typical structural adhesives need to be widely established, and pertinent data of this type need to be developed and documented as an important aid for aerospace designers and engineers in specifying improved performance of bonded joints in production applications. In addition, training programs need to be developed and initiated to inform such design engineers of the techniques and benefits in using such fracture mechanics data in better joint design.

Priority: High

#### 7.4.1.7 Environmental Interactions

Conclusion: Effects of environmental exposure of adhesive joints are, in general, poorly understood. The role played by agents such as water, and means of restricting sensitivity need better definition.

**Recommendation:** Mechanisms by which environmental agents such as water and water vapor affect properties of an adhesive and the strength of a joint should be the subject of expanded research. Attention should be given to both chemical and physical factors (e.g., degradation and plasticization) and to specific interfacial reactions. Mechanical studies should be coupled with chemical studies (e.g., by Raman spectroscopy) in order to clearly understand mechanisms of chemical failures.

**Priority:** Urgent

#### 7.4.1.8 Communication Problem

**Conclusion:** The technology of adhesive bonding does not seem to have taken full advantage of recent basic and applied developments in materials science, particularly the reinforcement of engineering plastics by means of composite structures such as rubber-toughened and fiber-reinforced formulations. Also, communication among different investigators in the general field of adhesives science and technology is inadequate.

**Recommendation:** Multidisciplinary cooperative research programs involving government research establishments, industrial organizations, and university research teams should be initiated to undertake the various research programs previously cited and to bring new experimental approaches to focus on adhesive performance problems of improved structural adhesive bonding maximizing knowledge already available from other areas of materials sciences.

**Priority:** Urgent

#### 7.4.2 Benefits

While cost-benefit analysis cannot be directly applied to long-range research, all the programs proposed should yield valuable technical results at minimum cost. Indeed, even a modest research commitment should yield large gains in basic knowledge and in the ability to apply such knowledge in view of the present limited state of development of basic information about adhesive properties in the joint. The following major, direct technological benefits may be anticipated as a result of the proposed programs:

- The aerospace designer will be able to design bonded joints more intelligently rather than so much on an empirical basis, as at present
- The materials engineer will be able to cooperate in a rational design plan with the designer and adhesive chemist to achieve maximum strength
- The chemist will be able to formulate adhesive systems to optimize joint strengths and service life on a rational basis
- Critical design factors will become clear so that more efficient and economical joint designs to meet specified requirements will be achieved

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## CHAPTER 8

DESIGN, ANALYSIS, AND TEST METHODS8.1 Purpose

This chapter covers the three principal areas of interest to structural design and analysis engineers engaged in utilizing structural adhesives for aerospace vehicles (i.e., design, analysis, and test methods). The types of adhesive bond considered include bonded laminates (various combinations of metal and/or filamentary composites), bonded sandwich constructions, and miscellaneous combinations of bonded plus mechanically attached structures. The purpose of this chapter is to summarize the present state of the art and then to identify some of the more important problem areas and indicate their respective possible solutions. Recommendations for future investigations, which should be conducted to resolve these problems, together with an estimate of the resulting benefits expected and priorities to be observed conclude this chapter.

8.2 State of the Art

The present generation of aerospace structures utilizing adhesives extensively has been built by fairly empirical methods, with a strong reliance on the pragmatic approach of designing and analyzing in accordance with simple standards and presumably common sense methods, building a structure or model, and then testing it to determine whether it meets the criteria for non-failure under simulated service conditions. If the structure failed prematurely, the weakness was reinforced and the design refined and retested repeatedly until the design criteria were met and the design was considered acceptable. This approach is no longer possible on future aerospace vehicles because the requirements for structural adhesives are becoming much more stringent because the adhesive user now has available many different adhesives that are capable of widely different performances, and because cut and try design is economically prohibitive today. Hence, to make possible the utilization of adhesives for their special design advantages and the rational design of more advanced structures, understanding of how to design



an adhesive joint must be significantly improved.

The purpose of this section is to review briefly the present status of structural adhesive bonding in the aerospace industry with regard to design, analysis, and testing in order to establish the foundation from which future developments must advance.

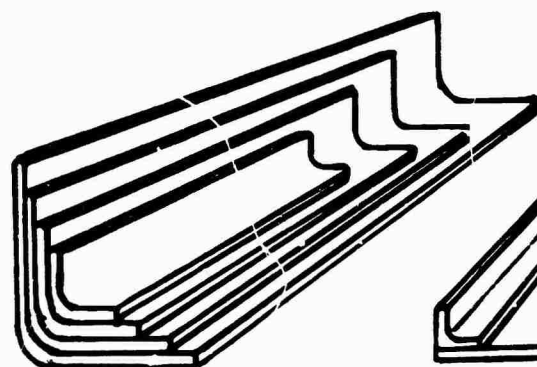
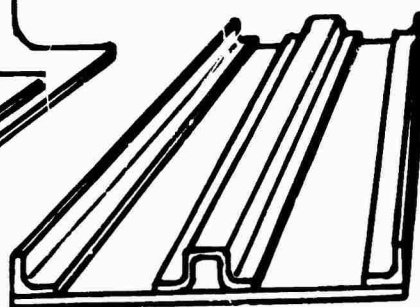
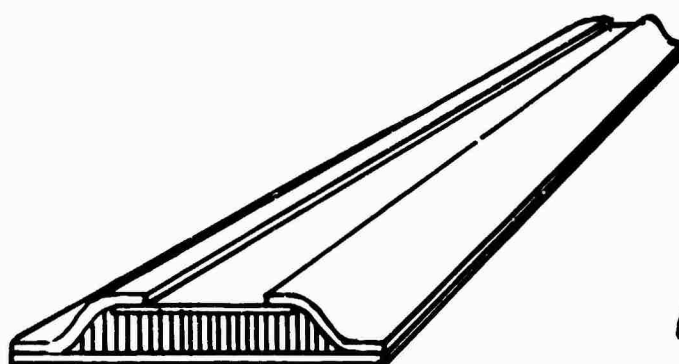
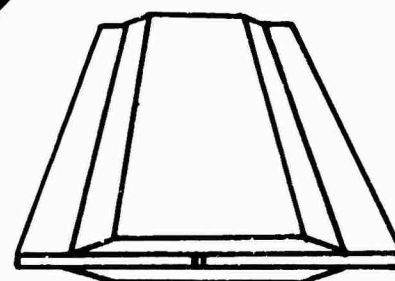
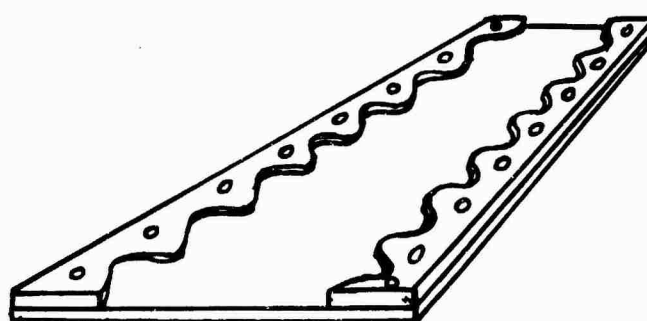
#### 8.2.1 Design

Present applications of aerospace structural adhesive bonding can be arranged into five general categories (Figure 31).

- Bonded laminates
- Bonded stiffeners
- Bonded sandwich constructions
- Bonded primary structural joints
- Bonded plus mechanically fastened structures

Usually the design and analysis efforts required for all but bonded primary structural joints are fairly simple and require little effort because the stresses and other demands on the adhesives are small as long as the bonded adherends do not begin to fail first and thereby induce peeling stresses in the adhesive.

The design of adhesive bonded aerospace structures involves establishing the design conditions and criteria, considering the adhesive and substrates to be employed, the size and dimensions of the bonded structure and the steps and costs that will be involved in tooling, processing, and fabricating. The design engineer must consider the type of structure, service requirements, mechanical strength factors, environmental degradation in service, and fabrication and inspection costs. These considerations are usually approached by analyses and by testing--laboratory, assembly test performance, or both. This may include environmental tests, service tests, and destructive and nondestructive tests.

**BONDED LAMINATES****BONDED STIFFENERS****BONDED SANDWICH  
SANDWICH****BONDED STRUCTURAL  
JOINT****BONDED PLUS MECHANICALLY  
FASTENED STRUCTURES****FIGURE 31 Five general categories of adhesive bonding**

#### **8.2.1.1 Bonded Laminates**

Doublers are bonded to thin skins to reinforce those areas where holes must be drilled or countersunk for rivets or other mechanical fasteners and where large openings, such as doors, windows, and other access holes, must be reinforced to reduce the effects of stress concentrations. Extensions of this type of bonding include strips bonded to fuselage skins to act as crack stoppers and either flat or contoured multiple-layered bonded sheets to form step-tapered plates or built-up shapes such as channels, angles, I-beams, and hat sections.

#### **8.2.1.2 Bonded Stiffeners**

Various shapes, such as angles, hat sections, channels, and beaded doublers, are bonded to thin skins to act as longerons or rings, and thereby increase stiffness and reduce general instability and buckling effects.

#### **8.2.1.3 Bonded Sandwich Construction**

Thin skins bonded to honeycomb, balsa wood, or foam type cores are very popular for applications where continuous skin support is needed.

#### **8.2.1.4 Bonded Joints**

The two types of bonded joint include closure joints, such as Z or channel members bonded to the four edges of a honeycomb sandwich, and the primary structure joint that is found where skins or longerons splice or at major structure intersections.

#### **8.2.1.5 Bonded Plus Mechanically Attached Structures**

Designers who are reluctant to replace riveting or spotwelding by adhesive bonding can use the adhesive for its ability to improve the parallel mechanical fastening method. For example, such combinations are reported to exhibit resistance to crack propagation and peel superior to that of either fastening method alone. Because the relative "stiffnesses" of these combined joining methods are quite disparate, when stressed to their ultimate, one of the fastening methods usually fails before the other has shared much of the total load.

### 8.2.2 Analysis

Recognizing that present aerospace design practice has not caught up with newer analytical techniques (see Chapter 9), present analysis efforts in aerospace structural adhesive bonding can be separated into three categories:

- Theoretical analyses of stresses and strains
- Experimental analyses
- Failure analyses

Most of the analysis work in all three categories has been concentrated on bonded lap joints, and the original pioneering work of Volkerson (1938) and Goland and Reissner (1944) has been continued and expanded during the past 30 years by other investigators (Cornell 1944; de Bruyne 1944; Goodwin 1963; Grimes et al 1971; Hahn 1960; Hart-Smith 1973 (refs. 11, 12, 13, 14, 15); Kutsch 1962; Mylonas 1948; Theodosiadis 1969). In a similar fashion, although not in as much detail, another line of investigation has followed the analysis of adhesive peeling (Kaelble 1960; Spies 1952; Yurenka 1961). The ultimate objective of these analyses has been to develop a design method for bonded construction, based on the principles of mechanics and rational engineering design so that joint behavior could be predicted.

#### 8.2.2.1 Theoretical Analyses of Stresses and Strains

Most theoretical analyses have been based on the single-, or double-lap-type joint because these are the most common types occurring in adhesive bonded assemblies. The analyses of scarf and stepped-lap joints are very different from lap joints and have rarely been attempted (but see Ripling et al. 1971). Lap joints also are the primary type of joint used for determining the strength of adhesive joints. There is a good reason for this reliance on a lap type configuration. If the joint is properly designed, the primary stress on the adhesive is a shear stress, toward which adhesives oppose their greatest strength. Adhesive joints are notoriously weak in peel and also are weak under tensile loads applied normal to the plane of the joint. The need for strong adhesives with high peel strength is still very acute.

The earliest theoretical lap joint work involved the most simplifying assumptions; i. e., the joint was a simple overlap type, both adherends were made of the

same metal and had the same geometry, the adherends and the adhesive behaved elastically, bending or peeling stresses were not included, thermal expansion or residual stresses were ignored, deflections were small, etc. Furthermore, the stress-strain distributions that were derived were "closed form" solutions of various differential equations.

Present theoretical efforts have become much more sophisticated. New computer-assisted techniques have introduced the application of finite element matrix theory type approach. Parametric studies are being conducted to determine the effects of important variables. Double-lap joints, scarf joints, joggled joints, and stepped-lap joints have been added to the original simple overlap joint and non-linear closed-form solutions are available (Hart-Smith 1973 (refs. 11, 12, 13, 14, 15)).

New adherend materials, especially the advanced filamentary composites, are now being considered and various bonded combinations of materials with different stiffnesses and various geometries have become common. The elastic, low deflection, constant temperature behavior of scarf and stepped-lap joints has been replaced by elastic-plastic, large deflection behavior combined with thermal expansion difference or curing shrinkage-induced residual stresses.

Many new considerations arise and promise to continue to complicate the analysis picture. Now the theoretical expert is supposed to handle fatigue, creep, impact, varying elevated or very low service temperatures, continued heating deleterious environmental effects, corrosion of the metal substrates, crack propagation, yielding of the adherend, and a host of other variables. Although theoretical analyses of bonded joints have progressed rapidly and far, the list of new unsolved problems continues to grow as the new problems are recognized and the old problems are resolved.

#### 8.2.2.2 Experimental Analyses

Whether a theoretical analysis is successfully completed or whether the practical complications outstrip the capabilities of even the most sophisticated approach, today the only conclusive verification remains the experiment. However, in this area of analysis progress has not been nearly as great because the labor and materials costs

associated with laboratory experiments surpass theoretical efforts manyfold and, hence, provide a very effective economic deterrent to significant progress in relating theory, laboratory test, and real-life performance. Typically, the yardstick for qualitatively measuring the internal resistance of an adhesive bond to an external load has been the determination of the strain distributions in the adhesive and the adherends. This is no small task. Even in the simplest lap joints, the actual stress-strain distributions under load are extremely complex combinations of shear and tensile stresses and are very prone to disturbance by non-uniform material characteristics, stress concentrations or localized partial failures, creep and plastic yielding, etc. The fact that the adhesive gage length (glue line thickness) is very small and that the adhesive is so completely encapsulated between the adherends that it is practically inaccessible means that the strains are both hidden and small and, hence, extremely difficult to measure accurately. The usual techniques of extensometers, strain gages, and photo-elasticity are being used with limited success.

#### 8.2.2.3 Failure Analyses

The function of a structural adhesive joint is to transmit an external load to the structural members. If the joint fails to function properly, it will undergo damage or failure. This damage could be actual fracture of the structure, excessive elastic deformation, or excessive inelastic flow. The criteria for what constitutes structural failure depend on the performance requirements of the joint. The fundamental problem in the mechanics of adhesives and of joints is to obtain some relationship between the loads applied to the joint and a parameter that will adequately describe the criteria for structural failure. For example, if a joint is considered to have failed when its elastic deflection reaches a certain limit, a relationship is necessary between applied load and

elastic deflection. Similarly, relationships may be necessary between joint strength and applied load or creep and applied load. The most common criterion for structural failure of lap type joints is actual fracture of the joint. For a given combination of adherend and adhesive, the stress analyst has to make a decision as to what the mode or theory of failure of the joint would be if the applied loads became large enough to cause failure. The decision as to which theory would realistically determine the mode of failure is usually based on past experience or some form of experimental evidence.

The selection of a failure theory for a particular adhesive joint then leads to the determination of a relationship between the applied load and a parameter (stress, strain, strain energy, etc.) that will describe the failure of the joint. Assuming, for example, that the joint will fail when the principal stress in the adhesive perpendicular to the plane of the joint (tensile stress) reaches a level sufficient to cause fracture, it is necessary to know the strength of the adhesive under tension in this direction when constrained by the adjacent adherends. Finally when maximum tolerable stresses have been obtained, the allowable stress values or factors of safety are decided upon to allow for factors such as long- and short-term loading, fatigue loading, special environmental conditions, and other special considerations. This step is usually based on experience, engineering judgment, and legal, government, or commercial specifications.

### 8.2.3 Testing

The performance of an adhesive in a joint is dependent upon the mode of loading of the joint. The most common and most desirable mode is in shear, and the tensile lap-shear test of an adhesive is used almost universally. The ease of fabrication of such a specimen accounts for its appeal. The specimens also lend themselves to economical test-

ing at elevated temperatures or low temperatures or after aging at various temperatures. However, because the bonded adherends are usually very thin, the stress distribution is so non-uniform that the data obtained from the standard lap-shear test (ASTM D1002-72) are questionable as adequate design values. This makes it difficult to derive a fundamental strength value independent of joint dimensions. The stress concentrations are reduced if the bending and stretching of the adherends are minimized by making them much thicker. Recently, Frazier (1970) and other investigators have independently developed a thick-adherend, lap-shear specimen and test that were reputed to have minimized the stress variation across the joint. Until recently (Frazier 1971), very little usable data were available in the literature on structural adhesives tested by this method and with complete stress-strain curves to failure. Parallel analytical derivations and experimental observations have reinforced the belief that the most important property of an adhesive in determining its relative usefulness in contrast to other adhesives is the area under its shear stress-strain curve to failure. This quantity is known as adhesive toughness, and recent work by Hart-Smith (1973) (ref. 11), has demonstrated that such toughness measurements can be used to evaluate and compare the load-resisting capabilities of lap joints bonded with different adhesives, bonding together adherends with various joint geometries.

Since 1968 there have been continuing studies of micromechanical properties of adhesive-bonded joints using extensometers (Bossler et al. 1968; Hughes and Rutherford 1968; Rutherford et al. 1968) sensitive to strains on the order of  $10^{-6}$  to  $10^{-8}$  inches per inch. This strain sensitivity has been sufficient to develop strength properties of adhesives that are directly usable to the designer. Stress-strain curves of adhesive-bonded joints tested in tension and shear have shown that typical structural



adhesives exhibit elastic, viscoelastic, and plastic deformation. Precise elastic limit, micro-yield stress, and elastic and shear moduli are typical properties measured. Further evaluation of this technique of characterization of structural adhesives is under way. Preliminary indications are that fatigue testing and durability testing will corroborate the significance of the stress-strain data for the design of more reliable practical structures.

In principle, a pure shear test is much better obtained if a bonded joint is subjected to torsion; hence, this test involves rod or tubular adherends bonded coaxially together. The latter design is sometimes called the "napkin ring" test (ASTM E229-70). It has the advantage that if the annular width is small compared to the diameter, the shear is practically uniform over the whole joint. The drawback to this test, which is confined to use in the research laboratory, is that the ring test specimens are expensive and difficult to fabricate accurately and reproducibly, and curing the adhesive in such a specimen at elevated temperatures may result in somewhat different film properties than in a typical lap joint between thin adherends.

The peel test also is considered to be indicative of the relative toughness of an adhesive. Three peel tests currently are used for metal-to-metal joints -- climbing drum peel (ASTM D1781-62), T-peel (ASTM D1876-72), and Bell peel (Ripling et al. 1971). Peel strengths are published for many adhesives; however, such testing is not nearly as extensive as for lap shear. Although a peel test is valuable in comparing the toughness of different adhesives, or for changes induced by varying temperatures, testing speeds, surface cleaning treatments, or other similar variables, its values are not directly usable by design engineers in their design analysis.

A requirement for adhesives that is receiving increasing emphasis is

a high degree of resistance to crack propagation. Several types of cleavage test have been proposed to measure this property (Ripling et al. 1971). Fracture mechanics and fracture phenomena in adhesive joints are considered in detail in chapter 7.

Fatigue, creep, stress rupture, and impact tests are generally conducted with a simple lap-shear test specimen, but the literature does not indicate that the thick adherend specimen has been used for these purposes.

The results of a number of shear fatigue tests can be expressed in the form of an S-N curve by plotting the alternating stresses versus the corresponding numbers of cycles to failure. Unlike ferrous metals that exhibit an endurance limit (i.e., a minimum alternating stress below which no failure occurs even after a very large number of cycles), adhesive-bonded lap-shear fatigue specimens have no horizontal asymptote in their S-N curves but instead continue to fail in fatigue even at low stresses after a large number of cycles. Hence, endurance limit for adhesive lap-shear test specimens is defined as the value of the alternating stress from an S-N curve corresponding to an arbitrarily selected large number of cycles, such as  $10^6$  or  $10^7$  cycles to failure.

A standard test method for sonic fatigue testing of bonded aircraft structures does not exist; ad hoc tests usually are conducted by mechanically connecting a bonded structural test panel of a particular design to an opening in the side of a rectangular duct through which the sonic impulses of an air-driven horn are conducted.

Adhesive-bonded sandwich constructions or panels with bonded stiffeners as shown in Figure 31 proved to be so much more resistant to sonic fatigue damage than the usual stiffened panel constructions in which rivets or screws were employed that the use of adhesive bonding

for jet aircraft structures has accelerated very rapidly.

In the case of bonded sandwich constructions, the flatwise tensile test provides the best test of the core-to-face adhesives (ASTM C297-70). This test is conducted by bonding blocks to the core in place of the face sheet and loading in the tensile mode or by bonding a block to the face sheet of a sandwich.

The climbing drum peel tester for metal-to-metal adhesives also is used to conduct peel tests of honeycomb sandwiches (MIL-STD-401 and ASTM D1781-70). This test utilizes a 4-inch-diameter cylindrical drum with cables or metal straps around larger flanges. One face sheet of the test sample is attached to the drum, and the force on the cable or straps necessary to pull the drum up and separate the face sheet from the core is continuously recorded. Although empirical, the drum peel test value has some relation to the risk of failure on a bonded flight structure if undetected voids or debonds are present.

### 8.3 Problem Areas

In this section, specific problem areas associated with the design, analysis, and testing of adhesive bonds for bonded aerospace structures are defined. In each case the problems discussed will be those associated with the adhesive bond, rather than the entire structure. The order in which the problems are arranged also is intended to provide a measure of their relative priorities. Wherever possible, an estimate of the ensuing benefits that will result from the satisfactory resolution of the problem area also is made.

#### 8.3.1 Design

For the design of adhesive bonds, the following specific problem areas are listed in order of their relative importance, with their

corresponding recommended solutions and estimates of resulting benefits

#### 8.3.1.1. Designer Reluctance to Rely on Adhesive Bonding

Problem Area: A universal complaint exists that design engineers are reluctant, if not openly resistant, to using adhesive bonding in the designs of their primary structures, in spite of its obvious advantages over other methods of fastening. The critics recognize that some of this reluctance is understandable (especially where it is based on uncertainties in cost, reliability, nondestructive inspection, difficulty in repairability, and low resistance to moisture and corrosion). However, they also believe that the designer fails to take advantage of design with adhesive bonding and to demonstrate enthusiasm and determination to solve or overcome such uncertainties in the use of structural adhesives by applying the necessary extra effort and ingenuity. The factors contributing to the aerospace designer's reluctance should be identified and then alleviated.

Recommendation: Screen available literature on the design of adhesive bonded joints; select the most suitable data, equations, criteria, theories, and design curves; and assemble these into a simple design guide in handbook form, that can be used by designers and analysts. Illustrate the design recommendations with solutions to typical sample problems. Either generate approaches and information that are needed but are not presently available, or else identify the absence and need for information, so that it may be added in later editions of the guide as it becomes available. In addition to bonded joints, the design guide also should contain sections devoted to bonded sandwich construction.

The existence of a design guide would minimize the time that each designer now has to spend to search, digest, and evaluate such information for himself and would help to eliminate the fear of the unknown that is

the basis for much of his reluctance.

#### 8.3.1.2 Specifications for Designers

Problem Area: Because each company or laboratory that utilizes adhesive bonding usually prepares its own adhesive standards, there are no universally accepted standard specifications for materials, processing, and tooling. These standards are generally available within each company and are fairly adequate. Section 5.4.1.2.1 of chapter 5, Manufacturing and Processing, recommends that specifications covering specific adhesive types and the bonding process "should be consolidated into a single set of procedures required for general industry use." However, a similar need exists for design specifications useful to designers of adhesive bonded structures. Unfortunately in this area of design much less preliminary information exists so that the need is even greater.

Recommendation: The major users and investigators of adhesive-bonded structures should be canvassed to collect available information or recommendations, and these should be assembled into a preliminary industry-wide design specification for adhesive bonded aerospace structures. Although this preliminary specification undoubtedly will not be entirely adequate, it should at least indicate the type and amount of information that is available and what needs to be generated.

In cooperation with existing technical societies and users concerned with adhesive bonding, one leading organization should be designated to accept the responsibility for generating the data required to provide the missing information. The preliminary specification should be enlarged, completed, and then circulated among the major aerospace users for their comments and additional recommendations. After a suitable trial period, this specification should be published as a federal specification and periodically reviewed and kept up to date. By combining the

efforts of many experienced organizations and societies in its preparation, this specification should benefit from a much wider applicability and acceptability than if it were prepared by a single organization alone. The availability to designers of such a specification should increase confidence in the reliability of adhesive bonded structures and enlarge application of adhesive bonding to aerospace vehicles.

#### 8.3.1.3 Composite Material-to-Metal Joint Design

Problem Area: Adhesive bonding has shown promise in lightweight joints in fibrous composites for specific applications. However, the joints with high-performance fibrous composites must sustain high loads to obtain maximum weight saving. The maximum loading of bonded metal joints has been limited by the shear strength of the adhesive; with fibrous composites the inter laminar tension strength in the composite is also a limiting factor. A knowledge of the optimum design of composite-to-composite or composite-to-metal joints made by bonding or a combination of bolting and bonding is required to design efficient composite airframe structures.

Recommendation: Investigate design techniques that will circumvent the low shear and tensile strength properties of the most promising composite materials applicable to aerospace applications. Possible approaches would be to modify the matrix with tough adhesives between the filament layers or to incorporate "softening strips" of thin specially shaped layers of "lower modulus" filamentary reinforcement between the structural filament layers and in the vicinity of the joints. The selection, design, and analysis of composite joints containing such adhesives, softening strips, or other equivalent approaches need to be placed on a rational basis.

If composite material structures are to realize their full potential,

the problem of their attachment to other components will have to be solved, primarily by means of adhesive-bonded joints.

#### 8.3.1.4 Design of Bonded Adherends with Dissimilar Coefficients of Expansion

Problem Area: Differences in the coefficients of thermal expansion between bonded adherends become important if the operating temperature is not the same as the bond cure temperature. If the thermal expansion of the adhesive is also different, as is generally the case, the problem is further aggravated. Any temperature change from the cure temperature causes thermal stresses in both the adhesive and the adherends. These stresses can cause bond failure, failure of the adherend materials, or unacceptable distortions of the joined materials. The "graded seal" concept is one proposed technique of relieving thermal stress problems when such materials as graphite composites, with their extremely small thermal expansion coefficients, are bonded to metals, such as steel or aluminum, with relatively large coefficients. Here, one or more thin layers of other suitable material ("seals"), which possess a thermal expansion coefficient intermediate between the two extremes are sandwiched into the bonded joints. In this way the residual strain differences are relieved in incrementally descending fashion.

Recommendation: The design solution, implicit in the "graded seal" concept, should be implemented by the selection of the optimum combination of "seals," adhesives, and their dimensions for various assemblies of adherends. Another technique that also might be considered is scarfing the joint in the load transfer area.

#### 8.3.1.5 Design of Bonded Adherends with Dissimilar Stiffnesses

Problem Area: When bonded joints between adherends that differ markedly in stiffness are loaded, the adhesive shear

strains are intensified at the end from which the less stiff adherends extend. In most bonded applications this has not been a problem because the adherends usually have been the same material. Recent and future aerospace applications, however, are leading to a wide gamut of bonded combinations of dissimilar materials in which this problem is serious. As in the case of the problem of bonded adherends with different expansion coefficients, when the adherends have different stiffness, the problem must be solved by "tailoring" the joint design so that it will best accommodate or ameliorate such effects.

Recommendation: It is recommended that all possible approaches to such tailoring of joint design be investigated including scarfing the stiffer adherends, local buildup of the softer adherend, incorporating two or more strips of different adhesives in the joint with the more ductile adhesive at the overlap edge of the stiffer adherend, or employing another variation of the 'graded seal concept."

Tailoring of the design of the joint to reduce the extreme strain differences in the adherends to a minimum would be of particular benefit to the technology of bonded composite structures that are now being bonded to various metals, but it also would be useful for improvements of bonded joints involving combinations of some of the newer advanced metals.

### 8.3.2 Analysis

The following specific problem areas, listed in order of their relative importance, with their corresponding recommended solutions and estimates of resulting benefits, are made for the analysis of structural adhesive joints.

#### 8.3.2.1 Theoretical Stress Analysis of Adhesive Bonded Joints

Problem Area: Although the theoretical analysis work done



on bonded joints to date is extremely valuable, much more remains to be done because each discovery has generally led to additional questions. Fortunately, the parallel development of new computer-assisted analysis techniques promises to lead to a more rigorous understanding of the stresses and strains in various types of bonded joints.

Recommendation: It is recommended that strong efforts be made to systematically obtain or refine and expand present theoretical closed-form solutions to differential equations that predict the stress distributions in the various types of bonded joints; i.e., single overlap, double overlap, stepped overlap, scarf overlap, and butt joints. These new or old solutions should be expanded to include cases in which the adherends are either the same or different in thickness and material, in which the adhesive and adherends exhibit either visco-elastic or plastic behavior, and in which temperature and thermal residual stress considerations can be superimposed on the static loads. Whenever the simpler closed-form approach does not lead to a satisfactory solution, finite element analysis techniques in combination with computer programs should be used. The applicability of such computer-based techniques to evaluate various more complicated adherend shapes and boundary conditions should be demonstrated.

As rapidly as new solutions to the various bonded joint problems are obtained and verified experimentally, they should be translated into design-type information that can be incorporated into the simultaneously evolving

"Design Guide for Adhesive Bonding". Also incorporate in the "Guide" the results of suitable parametric studies in which one parameter at a time is varied and the effects of its variation are isolated from other variables. Wider acceptance of adhesive bonding by structural designers would follow accordingly.

#### 8.3.2.2 Dynamic Analysis of Adhesive-Bonded Joints

Problem Area: A better understanding of the time-dependent or dynamic effects of stress on adhesive bonded joints, in terms of crack propagation, fatigue, creep, and impact, phenomena is needed in addition to static load effects.

Recommendation: In order to help establish criteria for predicting impending failure of structural joints, and thereby prevent catastrophic failures in service, it is recommended that when theoretical analyses of statically loaded, bonded joints are completed, studies be initiated without delay to extend or expand these analyses to include time-dependent (crack propagation, fatigue, creep, impact-fracture) effects as well. With regard to the fatigue analysis this should include both sinusoidal cyclic and random cyclic loading, as well as the type of deterioration and "fatigue" that an adhesive joint experiences when it is simultaneously exposed to various environmental stresses while it is being dynamically loaded. These environmental stresses should include long-time exposures to high and low temperatures, humidity and moisture, salt spray, sunlight, lubricating oils and other similar fluids or solvents. As far as possible these stresses should simulate an "accelerated" lifetime environment of the adhesive joint.

A knowledge of the intrinsic resistance of adhesives to various dynamic

and environmental effects would lead to development of more reliable designs.

#### 8.3.2.3 Adhesive Bond Failures

Problem Area: In most practical applications of adhesive bonded joints, the analysts and the designers do not concern themselves much with adhesive failures, crack propagation, and surface phenomena because it is their usual intention to so design and produce a component that, during the lifetime of its service, its adhesive joints will never be exposed to stresses sufficient to result in failure. In spite of these good intentions, however, adhesives do sometimes fail in service and therefore it is necessary to acquire both an understanding of the failure mechanism as well as the steps that must be taken to preclude its occurrence. Failure of adhesives in service is an especially bad feature that must be eradicated.

Recommendation: Theoretical analyses (verified by experiment) should be undertaken of the mechanics and modes of adhesive failures (by shear, tension, peeling, cleavage, loss of cohesion or adhesion) when subjected to static ultimate loads, impact loads, cyclic loads, creep loads, loads at various temperatures, and combined loads. Translate these findings into suitable design charts or graphs that can be used by designers in their designs of bonded components.

When adhesive bonds fail, some cost is involved. At the very least the part has to be repaired or replaced, but at worst this failure could lead to subsequent failure of the vehicle, failure of the mission, damage of other property, or the loss of human life. In this case the potential payoff may not be measured by some positive gain but rather by the absence of some negative loss.

### 8.3.3 Testing

The following specific problem areas, listed in order of their relative importance, with their corresponding recommended solutions and estimates of resulting benefits are made for the testing of adhesive bonds.

#### 8.3.3.1 Standard Shear Test

Problem Area: The present standard simple 1/2-inch-overlap shear specimen with 1/16-inch-thick adherends is universally used to obtain relative ultimate shear strengths of adhesives, but this is not suitable for generating shear stress-strain curves that can be used by designers in their designs of bonded joints. A need exists for a better specimen and test method that can be adopted as a universal standard for generating basic adhesive design data. The 1/2-inch-thick adherend lap-shear specimen has shown promise that it can retain the simplicity and low cost of the present method and also provide a much more uniform stress distribution and, hence, a more realistic stress-strain curve.

Recommendation: Studies should be undertaken on various geometric dimensions and other test variables for the thick-adherend lap test specimen to analyze and optimize the specimen designs, and an acceptable test specimen and method should be standardized. Acceptance of this recommended standard should be sought from ASTM and military agencies. Sufficient specimens should be fabricated and tested under various conditions to determine its degree of suitability and to generate some preliminary usable design data and true adhesive properties with adherend effects eliminated. The results should be compared with data obtained from "napkin ring" shear tests of similar bonded combinations.

The present literature contains an inadequate number of useable shear

stress-strain curves of structural adhesives obtained with the thick-adherend or the "napkin ring" shear tests and with extensometer readings to failure. As a result designers have been forced to rely on failure strength data obtained only from the present standard simple lap-shear test and to hedge their uncertainties with generous safety factors.

Development of a suitable standard test method and generation of more usable design data would permit greatly increased utilization of, and confidence in, adhesive bonding for aerospace structures. Because recent theoretical analyses show that adhesive thickness (inches) and shear strain (inches per inch) always appear in the numerator of mathematical expressions, it is possible to simplify the thick-adherend lap-shear test by reporting deflection rather than strain and ignoring thickness measurements.

#### 8.3.3.2 Measurement of Shear Strain

Problem Area: The usefulness of a standard or improved adhesive lap-shear specimen and test method would not be complete for providing the necessary design data on adhesives unless a better, precise method of measuring the shear strains in the adhesive film also was developed.

At least four types of extensometer have been employed by investigators for measuring adhesive shear strains; i.e., Kuenzi and Stevens (1963) employed a Martens mirror-type extensometer for "napkin ring" specimens at FPL; Zabora et al. (1971) utilized a similar optical telescope measuring device in tests at Boeing; Rutherford et al. (1968) developed a capacitance-type extensometer for butt tension and torsion shear tests at Singer; Frazier (1970) modified the mechanical portion of an inductance coil tension extensometer to a "zero gage length" thick-adherend shear extensometer and coupled its signal and that of the load

cell to an X-Y recorder which plotted a graph of shear load versus elongations. Nevertheless, each of these, and perhaps others, are all one of a kind with certain limitations and advantages over the others. None are commercially available, and if any aspiring investigator were to decide to conduct his own tests, he would first have to proceed through a similar time consuming and expensive trial and error extensometer evaluation and development program of his own.

Most present precision extensometers of the types previously noted are suitable only for tests at ambient temperature and are too delicate to survive the impact produced by a specimen's sudden failure. They must be removed just before the specimen fails. This means that the last part of the stress-strain curve is lost and that the entire test loses much of its value because it is the ultimate strain that serves as the failure criteria.\*

Recommendation It is recommended that an accurate shear strain extensometer be developed that is capable of measuring shear strains in test temperature ranges from -55 to 82°C and is rugged enough to withstand the impact and extreme expansion when a specimen fails. The electrical output of this extensometer should be combined with an autographic recording system that can plot the entire stress-strain curve to failure and also furnish a print-out from which information on elastic modulus, ultimate strength and elongation, and the area under the stress-strain curve to failure can be computed.

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\* But note recent work of Shirley Institute, Didsworth, Manchester, England, on high-impact strain gages (extensometers) (Jones 1973).

The combination of extensometer and stress-strain recording equipment should be developed and marketed commercially as additional equipment for present laboratory testing machines. Such equipment would not only reduce the present machine time specimen testing, but also would save the additional time spent by technicians in manually extracting needed design data from each stress-strain curve.

#### 8.3.3.3 More Accurate and Reliable Nondestructive Testing Techniques

Problem Area: A big challenge in the testing of adhesive joints is determining their performance and quality without actually failing them. This cannot now be done with any significant accuracy. The present state of the art of nondestructive inspection (NDI) of adhesive bonds is limited to finding porosity or voids by means of sonic, thermal, or other detection techniques and then making judgment estimates of their effects on loss of joint properties. Even if there were no voids or pores, but the adhesive was inadequately cured or the adherend surfaces were not cleaned properly, the bond would be poor and present NDI techniques are too limited to detect such deficiencies. A need for a simple accurate quantitative NDI instrument exists for precisely determining the relative strengths of joints of different qualities.

Recommendation: Either develop a new technique or refine a present technique that will lead to an acceptable NDI instrument and test method for quantitative determination of ultimate shear strength and elongation of adhesive joints. Incorporate an electronic system in the instrument to provide visible digital readouts of the desired design data.

This instrument would not only eliminate human error but also would greatly increase accuracy and, hence, reliability of the NDI test data; it

would save technician time now required to make such measurements manually.

#### 8.4 Other Problem Areas

Two general conclusions can be drawn from an overview of the present status of adhesive bonding in the aerospace industry as far as the areas of design, analysis, and testing are concerned: One is that all the information generated in these areas still is inadequate because the requirements for such information are outstripping the results of the progress made to date. The second conclusion, however, leads to a more serious concern; i.e., although there exist many individual examples of superior knowledge, gratifying enthusiasm, and brilliant success, there also exist much larger pockets of widespread ignorance, lethargy, and bitter failure. The problem stems from the usual difficulty of communication and slow progress in dissemination of even existing knowledge in a rapidly changing industry.

Taken together these conclusions suggest that if real progress is to be made in the advancement of adhesive bonding in the aerospace industry, it is not enough just to continue to spend more funds and effort in solving the many real problems that continue to arise; a part of these funds and efforts also must be devoted to the immediate dissemination of the knowledge gained. In the area of design, analysis, and testing, one such avenue of communication would be the universal design guide (previously discussed in paragraph 8.3.1.1 and perhaps patterned after the Air Force's Design Guide for Advanced Composites or some of the other Military handbook). If this result is combined with a continued effective distribution of circulated information stemming from symposia, short courses, reports, textbooks, movies, vendor data, etc., the hoped for results should be forthcoming.



Although many governmental agencies and private industrial users of adhesive bonding are aware of this information communication gap and have started some promising research work recently, the results may not be available soon enough to close it. If new research can be coupled with the increased reliance on modern scientific and computer-assisted design analysis and testing approaches, progress could be made more rapidly and with less wasted and repetitive effort. Then, too, adhesive bonding of aerospace vehicles has reached the level of maturity and acceptance at which deterrents to its use, such as skepticism, uncertainty, strangeness, and high costs, are no longer as serious and limiting as initially, and the state-of-the-art can continue to flourish from an established base. It is recommended that high priority be given to establishing and prosecuting well-chosen programs.

#### 8.5 Conclusions and Recommendations

This section summarizes the principal recommendations of this chapter and lists them in order of their relative importance, together with an estimate of the anticipated benefits.

1. Develop an Adhesive Design Guide and a universally acceptable adhesive design specification for use by aerospace designers and analysts. The availability of such a handbook and specification should have a very significant effect in rapidly increasing the effective utilization of adhesive bonding for the fabrication of aircraft and aerospace structures. (Priority -- urgent).
2. Establish and conduct well-chosen research and development programs to generate solutions to design problems in the design of bonded joints for advanced composites to metals, for materials with dissimilar coefficients of expansion, and for materials with different stiffnesses. Such solutions would extend the application

of adhesive bonding to several new important classes of dissimilar structural materials.

(Priority -- high)

3. Establish and conduct well-chosen research and development programs to generate solutions to problems in the static and dynamic analyses of the various types of bonded joints, and in the investigation of design crack propagation, and failure criteria of adhesive joints under various types of static, dynamic, or combined loads and at various temperatures and environments. This information would increase the reliability and extend the life expectancy of bonded joints.

(Priority -- high)

4. Establish and conduct well-chosen research and development programs to develop new standard test methods and instrumentation for the shear testing, crack propagation testing, and non-destructive testing of adhesive-bonded joints. Such methods and measuring instruments would increase the accuracy and reliability of test data and save the time and costs presently being expended by individual investigators who are each "reinventing the wheel."

(Priority -- average)

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## CHAPTER 9

### PERFORMANCE AND RELIABILITY

#### 9.1 Purpose, Definition, and Scope

This chapter is addressed to integrated test programs and test strategies for establishing the performance and reliability of adhesive-bonded systems. Earlier chapters in this report have included special considerations of adhesive selection, surface treatment and interface bonding, manufacturing processes, mechanical behavior, and joint design and testing. Performance and reliability in a bonded system is determined by the integrated resultant of these specific considerations.

Definitions that are pertinent to this discussion are:

- a. Performance -- a measure (or measures) of functional response relative to a preset design specification
- b. Reliability -- the mathematical probability that the design will function in accordance with the design specification over the service life of the structure

The major emphasis of performance and reliability testing is placed upon proof testing or service life testing for functional performance under conditions defined by the design specification. Accelerated test programs are by necessity used in the development of new designs. The objective of these test programs is to predict long-term performance and reliability based upon short-term tests under intensified conditions of performance degradation.

This chapter reviews the current status, problem areas, and potential areas for improvement in measurement and prediction of performance and reliability. Chapters 3 and 8 allude to the tremendous range of engineering applications for adhesive bonding in aerospace structures. Each application has a detailed design specification that must define a specific test program for performance and reliability. Rather than attempting to

discuss one or more of these specific application areas, this chapter examines the fundamental principles that apply to all test programs for performance and reliability.

## **9.2      Performance and Reliability Variables**

Predictive testing and analysis for performance and reliability of adhesive-bonded structures is presently in a dynamic state of development. Two recent reports by the National Materials Advisory Board (1970 and 1972) review important aspects of this subject.

The core concept common to all accelerated testing programs is the hypothesis that the rate of performance degradation is a systematic function of such stress variables as (Halpin and Polley 1967; Halpin et al. 1970.):

- a. Thermal stress
- b. Mechanical stress
- c. Environmental (chemical or corrosive) stress

Both the initial performance and the rate of performance degradation in adhesive joints are now understood to be related to the following variables (Tanner 1972):

- a. Design of the joint for the specific application
- b. Selection of adhesive materials
- c. Surface treatments
- d. Bonding operation process control
- e. Inspection procedures

Microfracture mechanics treats the cumulative damage processes of fracture as the resultant of the following variables (Kaelble 1971):

- a. Existence or nucleation of micro-defects
- b. Growth of micro-defects
- c. Coalescence of micro-defects
- d. Crack propagation and failure surface formation

The general description of stress, fabrication, and micro-mechanics

variables presented above serves to define the factors that predominantly influence the performance and reliability of adhesive bonded joints.

### 9.3 Design Considerations

Optimized performance and reliability in adhesive-bonded systems depend upon an implanted design concept. Figure 32 illustrates the design concept proposed by Epstein, Smullen, and Carter (1972). Initial design considerations require a well-defined study of adherend materials, loads, environment, and design constraints that specify the function of the bonded system. Fabrication variables listed previously in Section 9.2 appear as interdependent factors in the schematic of Figure 32. After the adhesive-bond process and detailed design configuration have been developed and tested, the quality control program assures reproducibility of the bonded system.

Performance and reliability are represented in the lower section of Figure 32 as the resultant of both the initial design considerations and the manufacturing process. Performance and reliability testing and analysis programs are thus conducted on the bonded system. The testing conditions are set to correlate with the loads, environments, and design constraints imposed in the initial design considerations.

### 9.4 Current Status of Predictive Testing

A recent report (NMAB 1972) defines a predictive test as any test that is useful in predicting the conditions of failure of a member or device. A predictive relation is defined as any relation that is useful in predicting the conditions of failure of a specimen. The conditions of failure include factors such as stress, temperature, time, number of cycles, and ambient environments (moisture, radiation, etc.). This same report lists the classes of tests in the following order of increasing complexity or specialization:

- a. Simple tests -- standard or conventional
- b. Simple non-conventional tests
- c. Component tests



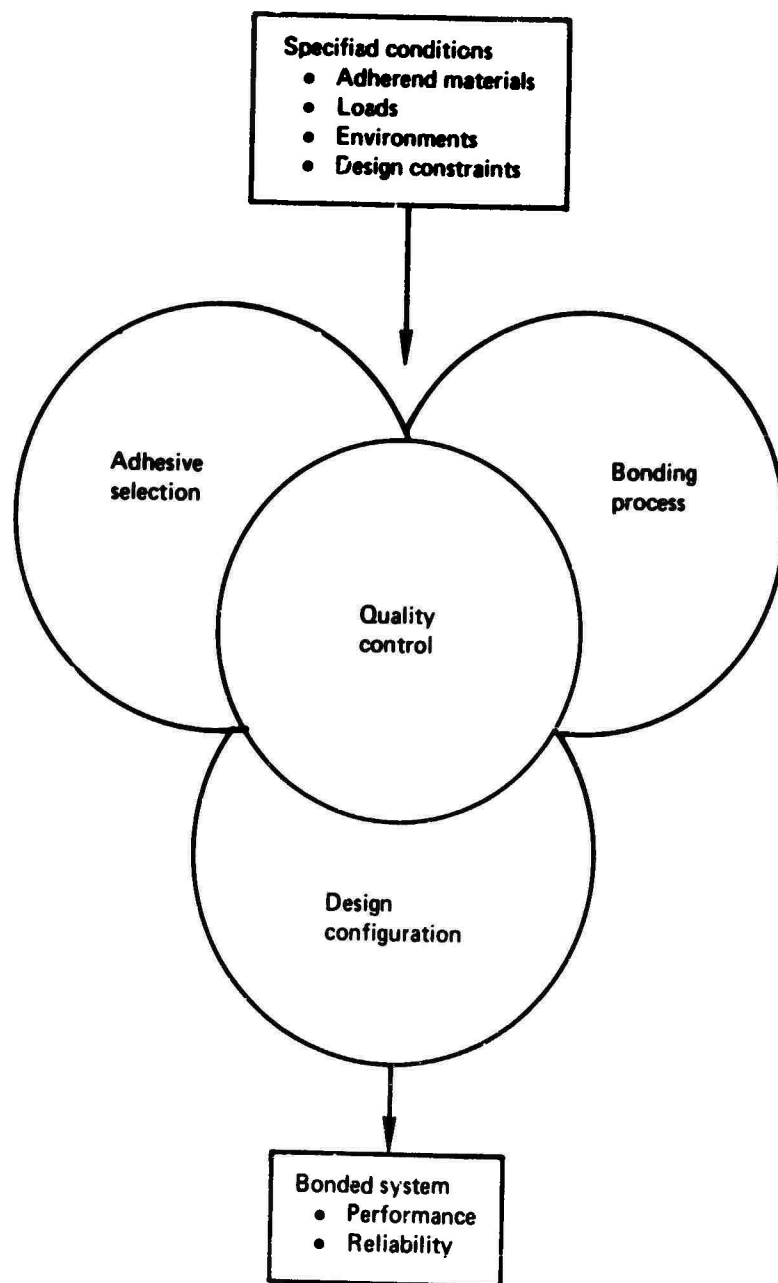


FIGURE 32 Design process for bonded systems.

**TABLE III: Outline for Detailed Analysis of Adhesive Bonding and Failure Mechanisms**

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- I. Interfacial Chemistry**
  - a. Adsorption mechanisms of adhesion**
  - b. Interdiffusion mechanisms of adhesion**
  - c. Ionic-covalent (chemical) mechanisms**
  - d. Effects of bond polarity on service life due to environmental interactions**
  
- II. Rheological factors in the individual phases affecting adhesion and failure**
  - a. Chemo-rheological mechanisms -- e.g., viscosity as a function of composition**
  - b. Viscoelastic mechanisms -- e.g., creep effects**
  - c. Shear and dilational mechanisms -- e.g., change of properties with strain**
  
- III. Mechanics factors of system response**
  - a. Critical fracture stresses and energies**
  - b. Definition of realistic failure criteria**
  - c. Modes of loading**
  - d. Definition of realistic thermal, pressure. and stress histories**
  - e. Measurement of failure kinetics under realistic histories of separate and combined stress and environmental exposure**
  - f. Correlation of data in terms of service life theory**
  - g. Correlation of data with nondestructive testing (NDT)**

- d. Simulated service ..
- e. Tests of the actual device
- f. Service performance recording

A rapid transition from easily conducted tests to increasingly complex testing programs occurs as one moves down this listing of test methods. This section is primarily concerned with assessing the current status of component tests and simulated service tests, items c and d, respectively, in the above listing. Tests in these categories are normally conducted under laboratory-controlled conditions.

A detailed analysis of the failure mechanisms in bonded systems requires quantitative knowledge of the relevant chemical, physical, and mechanical factors such as that outlined in Table III. This same information is essential to the proper design for a predictive test for simulated service life. The detailed elements of quantitative knowledge outlined in Figure 32 and Table III may be unavailable. In this case, predictive relations provide an independent basis for designing the predictive testing program. Section 9.8 reviews the mathematical approach to predictive testing for service life. The theories reviewed in Section 9.8 include:

- a. Chemical reaction rate theory
- b. Classical cumulative damage theory
- c. Statistical cumulative damage theory
- d. Physical chemistry theory of cumulative damage

A rapid transition from simple considerations to increasingly detailed systems of data analysis are encountered as one moves down the list of theories for predictive testing. A recently developed physical chemistry theory of cumulative damage (item d) now incorporates all of the fundamental propositions of earlier theories (Halpin and Polley 1967; Halpin et al. 1970.).

#### 9.5 Problem Areas

One of the acute problem areas identified by current long-term

studies of structural adhesive joints (Lewis et al. 1971; McBee et al. 1972.) is a well-defined need for better understanding of the interfacial and rheological mechanisms of aging in bonded systems. The adhesive supplier can provide technical leadership by furnishing more information on the structural endurance of adhesive joints made with his product. New performance and reliability criteria that are defined in the context of systematic analysis for service life need to be adopted by both the adhesive supplier and user. Accelerated aging programs for simulated service life must anticipate the effects of mechanical, thermal, and environmental stressing. Presently, data demanded by the detailed outline of Table III are lacking for many adhesive systems employed as engineering materials in aerospace structures.

The requirement for "real time" testing of structural survival life of adhesive bonded components in aerospace structures carries with it the technical penalty that newly developed adhesives may not be utilized in currently designed aerospace systems. Consider the case of an aerospace vehicle under current design (year 1972) with a designated service life of 10 years. By requiring real time data for survival life, it follows that only materials developed and subjected to survival life testing prior to 1962 would be qualified for introduction into the current vehicle design. The reliability advantage (based on experience) obtained by utilizing such vintage materials must be weighed against the technical penalty of limiting the structural design by only incorporating the developments of older technology.

There is, admittedly, no presently developed science and technology of accelerated testing that fulfills the complex requirements for tracking and predicting service life for materials and adhesive bonded structures for aerospace applications. To provide effective tracking and prediction of long-term damage based upon short-term testing, the statistical and physical chemical concepts of cumulative damage (see Section 9.8) as expressed by thermal, mechanical, and environmental acceleration factors need to be fully

exploited. The fundamental issues dealt with in predictive testing and analysis are:

- a. The merits, reliability, and range of valid application of systematically designed studies of accelerated cumulative damage
- b. The ability of such studies to reveal the micro-mechanisms of damage

Both issues figure prominently in the valid application of accelerated testing as a means of replacing real time testing. In fact, it should be anticipated that careful analysis of a systematically designed program of accelerated testing can provide detailed information concerning the micro-mechanisms of the failure process that is not revealed by real time testing. The principles that will produce high intrinsic reliability in a systematically designed test program for accelerated service life are that:

- a. The time factors by which the test system accelerates the damage mechanisms should be based upon rational scientific principles
- b. The test system and associated analysis should reveal the physical-chemical nature of the damage mechanism
- c. The analysis of accelerated test data should suggest remedial means for retarding or preventing the damage effect
- d. The analysis of accelerated test data should provide quantitative data on system reliability (as defined by the Weibull cumulative distribution function in Section 9.8)

Until these requirements are met, the materials specialist who deals with new adhesives or bonding processes cannot blame the design engineer for demanding real time performance data.

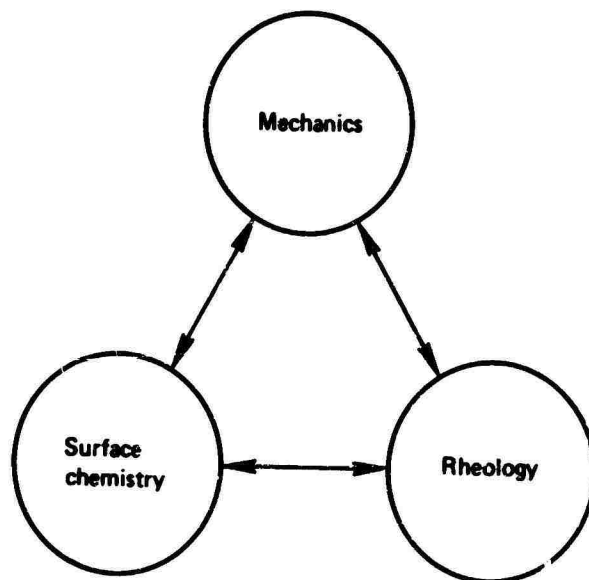
## 9.6 Potential Areas for Improvement

Discussion of the previous sections has pointed out that predictive testing and analysis for performance and reliability is presently in a state of dynamic development. A scheme for detailed analysis of adhesive bonding and failure mechanisms, as outlined in Table III, describes the interfacial chemistry, rheological, and mechanics aspects for performance and reliability. Some elements of the outline are present in all predictive test programs for performance and reliability. Unfortunately in present studies one rarely sees evidence that all of the elements are introduced into the scheme of predictive testing and analysis.

One fundamental reason for present information gaps in predictive testing and analysis programs is the inherent tendency toward arbitrary simplification and specialization of approach. T. C. Chamberlain in 1889 presented a paper entitled "The Method of Multiple Working Hypothesis," which has been reprinted recently (Chamberlain 1965) due to its relevance to complex research problems of present times. Prior to the newer guidance strategies for conducting complex research or evaluation schemes (Box 1954; Eisner 1962), the method of multiple working hypothesis (MWH) remained largely academic. Modern data analysis procedures (McAbee and Levi 1967 and 1969) now make the storage, selective organization, and processed retrieval of broad-ranged data both feasible and practical.

Present theories of adhesive bonding and failure (Kaelble 1971) show that the presently separated branches of the science of adhesion, depicted in the upper schematic of Figure 33, can now be integrated into a more highly unified context, as shown in the lower schematic of Figure 33 which defines as a central issue in the analysis scheme the molecular physics aspects of interfacial bonding. Both the thermodynamic and kinetic aspects of surface chemistry and rheology contribute to the identified theory of the interface (circle a). Rheology and mechanics analysis interact at the micro scale to provide a more detailed

## PRESENT STATUS



## DEVELOPING SYSTEMS ANALYSIS STATUS

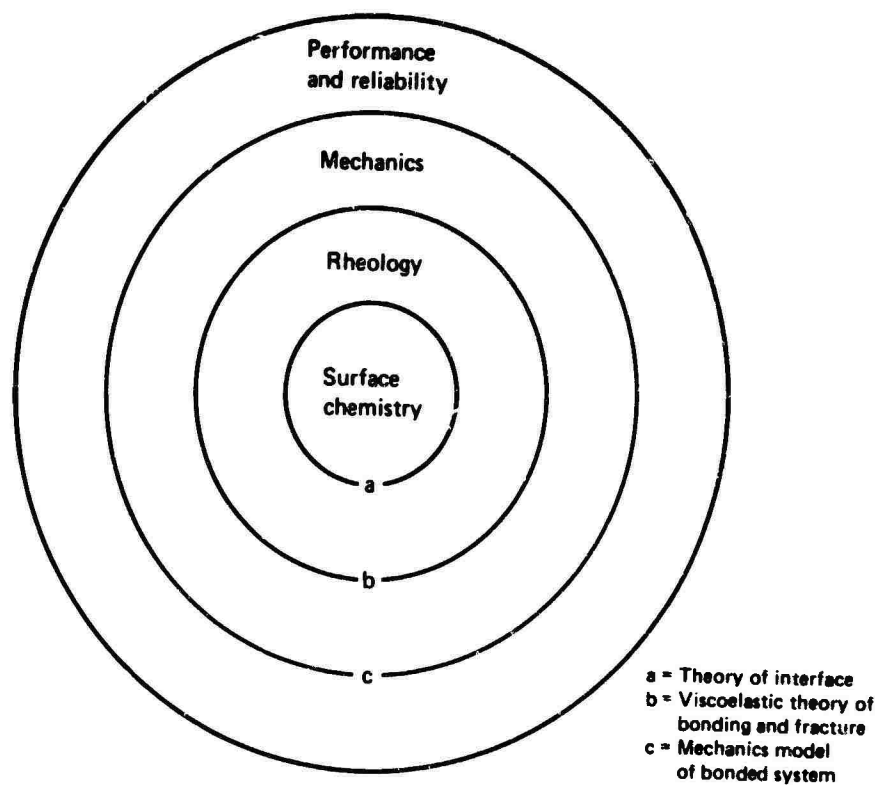


FIGURE 33 Correlation of scientific disciplines contributing to the rationalization of performance and reliability in adhesive bonded systems.

viscoelastic theory of bonding and fracture (circle b). Finally, mechanics analysis combines with performance and reliability analysis to define the relation of macroscopic performance and micro-mechanisms of failure in terms of the mechanics model of the bonded system (circle c). The detailed analysis scheme of Table III is thus diagrammatically reconstructed and presented as a superposition of considerations in the lower schematic of Figure 33.

An evident failure in present studies of performance and reliability is the special emphasis placed upon a singular aspect of the three separated subjects identified in the upper diagram of Figure 33. The systematic design and analysis of predictive testing for performance and reliability requires the application of recently developed statistical and physical chemistry concepts of system response (see Section 9.8). The analysis needs to be further detailed in terms of:

- a. Interfacial chemistry
- b. Rheological factors
- c. Mechanics factors

as summarized in Table III or the lower schematic of Figure 33.

Both the adhesives supplier and user would benefit from high reliability studies of service life for adhesive-bonded systems. New paths of communication could be developed between the design engineer and the materials development specialist that should substantially reduce the delay time in the introduction of new adhesive materials into primary structural applications in aerospace systems. The implementation of broader theoretical viewpoint (Chamberlain 1965) and modern methods of program optimization (Box 1954; Eisner 1962) appear as feasible augmenting factors in achieving this desired result.

## 9.7 Conclusions and Recommendations

### 9.7.1 Purpose, Definition, and Scope

Conclusion: General statistical and physical chemistry theories of



cumulative damage have recently been developed which largely replace classical cumulative damage theory and chemical reaction rate theory. These should be applied to structural adhesive bond design.

Recommendation: These theories should be more extensively tested, understood, and applied in performance and service life testing of structural adhesives in joints of various adherends and joint designs.

#### 9.7.2 Performance and Reliability Variables

Conclusion: Accelerated testing of structural adhesives in joints needs to be placed on a rational scientific basis in order to increase the reliance of design engineers on predictions of long-term damage based upon short-term testing.

Recommendation: Since direct application of the physical chemistry theories of cumulative damage provides a basis for improving the scientific design of accelerated test programs for structural adhesives, these theories should be exploited to establish their validity for designing reliable accelerated service tests and to establish when these tests should be used.

#### 9.7.3 Design Considerations

Conclusion: A quantitative definition of system reliability is mandatory in all accelerated testing programs for service life prediction. Older (Gaussian) methods are imprecise.

Recommendation: In predicting service life from accelerated testing data, exploit the Weibull cumulative distribution function (see Section 9.8) which represents a significant advance over standard analysis via the normal (Gaussian) distribution function.

#### 9.7.4 Current Status of Predictive Testing

Conclusion: The potential failure mode(s) of adhesive bonded systems due to reactions at the interface needs to be factored into accelerated testing design and analysis.

Recommendation: The mechanisms of interfacial bonding (see

Chapter 5) and potential environmental failure modes need to be considered in the design of service life tests. A theoretical analysis should be made to show how this may be done and damage (failure) equations modified accordingly.

#### 9.7.5 Problem Areas

Conclusion: Improved performance and reliability in newly defined applications for adhesive bonding (see Chapter 3) is an evident requirement.

Recommendation: A coordinated interdisciplinary application of concepts of adhesive bonding and performance analysis (see Table III) provides distinct advantages over present trial and error methods. Such analyses should be made in the selection of materials to implement design proposals.

#### 9.7.6 Potential Areas for Improvement

Conclusion: The kinetic mechanisms of moisture induced-failure (see Section 3.2.1.1) presently limit many applications of structural adhesive bonding.

Recommendation: Apply the physical chemical theory of cumulative damage (see Section 9.8) and the coordinated concepts of adhesive bonding and failure mechanisms (see Table III) to develop logical design parameters.

#### 9.7.7 Conclusions and Recommendations

Conclusion: Higher performance and reliability reduce repair costs (see Chapter 6) and extend service life (see Chapter 3).

Recommendation: A detailed survey by the Department of Defense should be made to define the economic and strategic benefits of increased performance and reliability in specific categories of design specifications for bonded structures.

#### 9.7.8 Appendix: Predictive Relations for Service Life

Conclusion: Improved flow of information between adhesive manufacturers and users on the results of accelerated service life testing is required.

Recommendation: Besides other conferences, Picatinny Arsenal in its dual role as a structural adhesives information center (see Chapter 10) and

center of adhesives research should sponsor symposia on accelerated test methods, performance and reliability analysis, and publish periodic reviews by authoritative experts in the field of adhesive and adhesive bonding technology.

#### 9.8 Appendix: Predictive Relations for Service Life\*

The essential point of this section is to briefly indicate that theoretical and experimental techniques are already developed and available to exploit the physical and statistical theories of failure. The specific physical property to be measured should correlate in some direct fashion with the discrete application of the materials. Ideally some discrete physical-chemical property of the system undergoing accelerated aging should be the measured variable of response. In practice this ideal cannot always be realized, and a complex physical response which correlates with performance may be selected.

##### 9.8.1 Chemical Reaction Rate Theory

Chemical reaction rate theory is generally considered as the simplified basis for relating time and temperature in predictive testing. Stated mathematically, reaction rate theory provides the following Arrhenius relation:

$$t_b = A \exp(\Delta H/RT), \quad (1)$$

where  $t_b$  = time (to failure),  $\Delta H$  = activation energy,  $T$  = absolute temperature,  $A$  = reaction rate constant, and  $R$  = gas constant. Taking logarithms one obtains the predictive relation:

$$\ln t_b = \ln A + \Delta H/RT. \quad (2)$$

equation (2) predicts that the logarithm of service life time,  $\ln t_b$ , varies linearly with the reciprocal of absolute temperature ( $1/T$ ) when other variables such as mechanical and environmental stress are held constant. This predictive relation presents the fundamental information that logarithmic time (or number  $N$  of loading cycles at constant frequency), rather than linear time, is the proper scaling factor. The second fundamental statement from equation (2) is that

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\*Personal Contribution, D. H. Kaelble.

increasing temperature diminishes  $\ln t_b$  while decreasing temperature extends  $\ln t_b$ .

Tobolsky and Eyring (1943) extended the above treatment by considering time (to failure) of a material subject to mechanical load to be governed by reaction rate theory. One form of the Tobolsky-Eyring relation may be written as follows:

$$t_b = (A/T) \exp [(\Delta H - \beta \sigma)/RT], \quad (3)$$

where  $t_b$  = time (to failure),  $\Delta H$  = activation energy,  $\sigma$  = applied stress (tensile or shear),  $T$  = absolute temperature,  $A$  = reaction rate constant,  $\beta$  = a constant with dimensions of volume/mole, and  $R$  = gas constant. Taking logarithms one obtains the following predictive relation:

$$\ln t_b = \ln (A/T) + (\Delta H - \beta \sigma)/RT. \quad (4)$$

Equation (4) predicts that at constant temperature,  $T$ , the logarithm of service life time,  $\ln t_b$ , varies linearly with the applied stress. This more general predictive relation shows that logarithmic time (or number of constant frequency cycles) is the proper time scaling factor. Increased stress,  $\sigma$ , is predicted to diminish  $\ln t_b$  and decreased stress to extend  $\ln t_b$ . The introduction of the  $\ln (A/T)$  term in equation (4) only slightly modifies the prediction of temperature effects on  $\ln t_b$  as stated earlier by equation (2).

Equation (4) can be considered as a reasonable basis for an empirical design and analysis of predictive tests for service life. Modified forms of Eq. (4) have been applied to analyzing the service life of structural adhesive joints under constant stress and constant strain rate loading in tensile lap shear (McAbee and Levi 1967; McAbee et al. 1970 and 1972.). For bond failure studies over an extended range of test temperature it is often found that either equation (2) or (4) fails to correctly predict the temperature dependence of  $\ln t_b$ . The reasons for this failure of the classical reaction rate theory are physically explained by the free volume theory of polymer viscoelasticity (Ferry 1971; Kaelble 1971.), which suggests a modification of equation (4) which has the following

form:

$$\ln t_b = \ln (A/T) + (\Delta H - \beta\sigma)/R(T-T_o), \quad (5)$$

where  $T_o = 0K$  for temperatures and stresses well below the glass transition temperature,  $T_g$ , of the polymeric adhesive. Recent studies (Clarke 1972) in climbing drum peeling of structural adhesive bonds shows that at test temperatures above  $T_g$  the value of  $T_o \approx T_g - 52K$ , while at temperatures below  $T_g$ ,  $T_o = 0K$ , as defined in equation (4). The result correlates with the more detailed description of two types of viscoelastic response in polymeric adhesives (Clarke 1972). Equation (5) introduces the important consideration that adhesive rheology can play a fundamental role in design and analysis of predictive testing for service life.

The chemical reaction rate theory approach to the design and analysis of predictive tests suffers from two outstanding deficiencies which are:

- a. Little detail concerning the actual failure mechanism is presented
- b. No independent analysis of the reliability (probability distribution for failure) is presented

These deficiencies in the reaction rate theory method have led to new statistical approaches involving concepts from the theories of cumulative damage.

#### 9.8.2 Classical Cumulative Damage Theory

The subject of cumulative damage in metals due to fatigue loading serves as a well documented area of both experimental and theoretical effort to track and predict service life. Current cumulative damage theories for simple or complex cycling loading are reviewed by Leve (1969). While a number of more recent theories are proposed, Leve recommends the application of an early theory of cumulative damage due to Miner (1945). The theory of Miner is based upon the linear damage concept; his essential assumptions are:

- a. Each group of sinusoidal stress cycles contributes a degree of damage determined by the linear cycle ratio of the group
- b. The damage accruing from any group is independent of the group location in the total stress history
- c. The total accumulated damage is equal to the sum of the damages contributed by each group

The mathematical statement of these propositions is outlined in the following failure criterion:

$$\sum_{q=1}^h \frac{n_q}{N_q} = 1.0, \quad (6)$$

where  $q = 1, 2, \dots, h$  describes the number of distinct sinusoidal stress groups,  $n_q$  = number of cycles in stress group  $S_q$ , and  $N_q$  = total number of cycles to produce failure in the cyclic stress condition  $S_q$ . More normally the present use of Miner's cumulative failure criteria involves the following modification (Leve 1969):

$$\sum_{q=1}^h \frac{n_q}{N_q} = K, \quad (7)$$

where generally speaking  $K \neq 1.0$ , and for conservative application  $K \approx 0.3$ .

Miner's rule -- as equation (6) or (7), has come to be known -- states the simplest possible propositions concerning cumulative mechanical damage in metallic materials under sinusoidal stress loading. Expanding the definition of stress to include time, temperature, and chemical or environmental stress provides the problem faced in generalized studies of cumulative damage histories.

It is generally observed that higher temperature and lower frequency tend to reduce both the fatigue life as measured by  $N_q$ , and the fatigue strength of both metallic and non-metallic materials. The effects of temperature and

frequency upon cumulative damage may be interrelated by relations which treat the effects of thermal activation upon material response. The studies of Daniels and Dorn identify a relation which presents this important proposition for metal fatigue as follows (Dorn 1961; Yen 1969.):

$$N_F = f(\omega e^{\Delta H/RT}, \sigma), \quad (8)$$

where  $N_F$  = number of cycles to failure,  $\omega$  = cyclic frequency,  $\Delta H$  = thermal activation energy,  $R$  = gas constant,  $T$  = absolute temperature,  $\sigma$  = stress, and  $f$  = an experimentally determined function. Equation (8) states that at a constant stress the same number of cycles,  $N_F$ , can be sustained at constant  $\omega \exp(\Delta H/RT)$  where higher frequencies,  $\omega$ , are equivalent to lower temperature  $T$ . Equation (8) implicitly defines the manner by which temperature, stress, or other control variables of a cumulative damage experiment may be applied to accelerate the cumulative damage processes. (But it should be noted that Miner's law does not necessarily hold for polymers -- certainly doesn't if  $\omega$  is high. Also, frequency effects in fatigue may be very complicated.)

### 9.8.3 Statistical Cumulative Damage Theory

The statistical cumulative damage concept of failure assumes that any disturbance during the lifetime of a specimen contributes to the eventual failure of that body. In engineering design the statistical theory that describes the minimum quality or minimum service life is often emphasized. This statistical description of minimum service life is termed extreme value theory and is applied to describe such varied phenomena as mechanical fatigue life, duration of human or other lives, radioactive emission, wind loading, and rainfall (Yen 1969.). A special formulation of extreme value theory is represented by the Weibull frequency distribution (Weibull 1961.) which assumes that failure is initiated at the "weakest link". The service lives of a group of specimens tested under a given set of conditions can be represented by the Weibull frequency distribution function:

$$f(N) = \frac{b}{N_a - N_o} \left( \frac{N - N_o}{N_a - N_o} \right)^{b-1} \exp \left[ - \left( \frac{N - N_o}{N_a - N_o} \right)^b \right], \quad (9)$$

where  $N$  = specimen life,  $N_o$  = minimum life  $> 0$ ,  $N_a$  = characteristic life at 36.8 percent survival of the population [ $36.8/100 = 1/e$ ,  $e = 2.718$ ],  $b$  = shape parameter of the Weibull distribution curve = slope of the Weibull cumulative distribution curve.

To simplify Eq. (9) let:

$$x = \frac{N - N_o}{N_a - N_o},$$

so that Eq. (9) may be written as:

$$f(N) = \frac{b}{N_a - N_o} x^{b-1} e^{-x^b}. \quad (10)$$

When  $b = 1.0$ , Eq. (10) provides a simple exponential distribution function:

$$f(N) = \frac{e^{-x}}{N_a - N_o}. \quad (11)$$

Setting  $b = 2.0$  provides the familiar Rayleigh distribution function:

$$f(N) = \frac{2x e^{-x^2}}{N_a - N_o}. \quad (12)$$

Setting  $b = 3.57$  provides a good approximation to the normal distribution function where the mean and medium values are equal:

$$f(N) = \frac{3.57 x^{2.57} e^{-x^{3.57}}}{N_a - N_o}. \quad (13)$$

Curves of the Weibull distribution functions for  $b = 1, 2, 3$ , and  $3.57$  are presented in Figure 34 in terms of  $f(N) = 1/(N_a - N_o)$  versus  $x = (N - N_o)/(N_a - N_o)$ .

For the purposes of this discussion the Weibull cumulative distribution function is of particular significance. The cumulative function for the fraction of samples failed,  $F(N)$  at lifetime  $N$ , is obtained by integration of



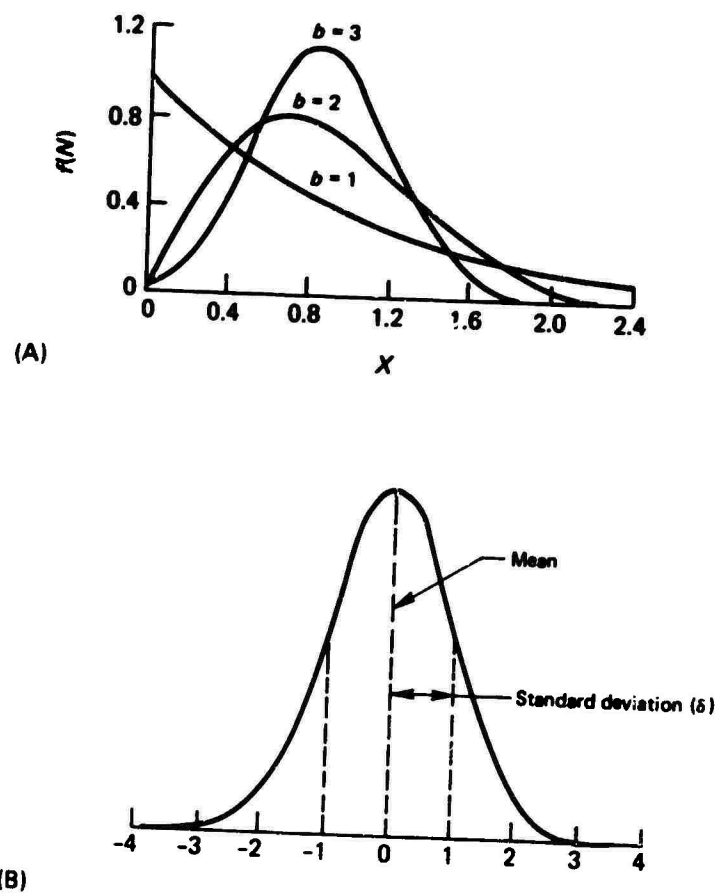


FIGURE 34 The Weibull frequency distribution function (A) and a normal distribution curve with  $b = 3.57$  in Weibull distribution (B).

$f(N)$  in Eq. (9) which provides the following expression:

$$F(N) = 1 - \exp \left[ - \left( \frac{N - N_0}{N_a - N_0} \right)^b \right]. \quad (14)$$

Equation (14) can be transformed into a linear relation by taking double logarithms to provide:

$$\log \log \frac{1}{1-F(N)} = b \log \left[ (N - N_0) / (N_a - N_0) \right] - 0.3622 \quad (15)$$

Plotting Eq. (15) as a linear relation of  $\log \log [1/(1-F(N))]$  versus  $\log [N - N_0]$  permits graphical estimation of the parameters  $b$ ,  $N_0$ , and  $N_a$  (Yen 1969; Weibull 1961.). Since the Weibull distribution has three adjustable parameters, it normally fits experimental data with greater precision than the normal distribution function which contains only the mean value and standard deviation as adjustable parameters.

#### 9.8.4 Physical Chemistry Theory of Cumulative Damage

A chemical-physical interpretation of the Weibull cumulative distribution function as it applies to the tracking and prediction of mechanical failure has recently been introduced by Halpin and co-workers (1967 and 1968). Halpin and Polley (1967) describe a viscoelastic material with pre-existing microscopic defects. These defects can be envisioned as flaws, dirt particles, etc., which randomly permeate the material. In the initial slow stages of flaw growth, the system is in a condition of quasi-equilibrium with the stresses at the flaw tip increasing as the radius of the flaw increases. Eventually the radius of the crack tip reaches a sufficient dimension that the stresses reach the critical value wherein rapid crack extension leads to sample rupture. This initial or slow growth stage of flaw extension is considered to contribute dominantly to the total time of failure,  $t_b$ . The specific values of the stress,  $\sigma_b$ , and strain,  $\epsilon_b$ , at rupture are thus directly related to the non-linear viscoelastic response at that time,  $t_b$ . For a three-dimensional flaw growth process the instantaneous defect volume,  $v(t, \theta)$ , is described by the following

expression:

$$v(t, \theta) = f[G_x G_y G_z (t-\theta)^3], \quad (16)$$

where  $f$  = an experimentally determined function,  $G_x, G_y, G_z$  = growth rates in the  $x, y, z$  dimensions which are assumed time independent,  $t$  = current time, and  $\theta$  = time of test initiation. For defect growth in one dimension -- as described by micro-crack extension -- equation (9) is modified to describe the instantaneous defect length,  $c(t, \theta)$ , by the following relation:

$$c(t, \theta) = f[G_x Y_y Y_z (t-\theta)], \quad (17)$$

where  $G_x$  = the growth rate along the  $x$  axis of flaw extension and  $Y_y, Y_z$  = fixed flaw dimensions in the axis of zero growth. These preliminary statements concerning the dimensionality of slow micro-flaw growth are combined to provide the following general statement concerning the cumulative survival distribution function  $F(S)$  for the material:

$$F(S) = \frac{n(t)}{n(\theta)} = \exp \left[ - \frac{K G (t-\theta)^b}{a_T a_M a_c} \right], \quad (18)$$

where  $F(S)$  = fraction of original specimens remaining intact at time  $t$ ,  $n(t)$  = number of specimens remaining intact at time  $t$ ,  $n(\theta)$  = original number of specimens at the time of test initiation  $t = \theta$ ,  $K$  = material or system constant relating to the ratio of stress to relaxation modulus,  $G$  = generalized flaw growth rate (assumed constant for a given test geometry),  $a_T$  = dimensionless time shift factor relating to temperature effects,  $a_M$  = time shift factor relating to level of mechanical stress (or pressure),  $a_c$  = time shift relating to chemical, corrosive, or environmental effects,  $b$  = exponent of time relating to dimensionality of the crack growth process ( $b = 1, 2, 3$  is correlated with one, two, or three dimensional flaw growth. Non-integer values of  $b$  relate to competing types of flaw growth),  $t$  = current time, and  $\theta$  = time of test initiation. Taking logarithms of equation (18) one obtains:

$$-\log F(S) = 0.4343 K(t-\theta)^b / a_T a_M a_c$$

$$\log[-\log F(S)] = b \log(t-\theta) + \log GK/a_T a_M a_c - 0.3622. \quad (19)$$

Plotting equation (19) as a linear relation of  $\log [-\log F(S)]$  versus  $\log (t-\theta)$  provides the slope,  $b$ , which relates to the geometric dimensionality of the failure growth process.

The correlation between equation (19) and equation (14) is obtained by recognizing that:

$$F(S) = 1 - F(N); \quad (20)$$

whereupon, Eq. (14) can be rewritten as:

$$\log[-\log F(S)] = b \log x - 0.3622. \quad (21)$$

The slope,  $b$ , of the Weibull cumulative distribution function is correlated with the failure dimensionality parameter of the theory of Halpin. The parameter,  $x$ , in the Weibull distribution function is reidentified by the Halpin theory as:

$$x^b = (t-\theta)^b GK/a_T a_M a_c, \quad (22)$$

where time shift factors  $a_T$ ,  $a_M$ , and  $a_c$  for the respective temperature, corrosive, or mechanical activation processes are isolated.

The physical interpretation of the time shift factors  $a_T$ ,  $a_c$ , and  $a_M$  in the Halpin theory reveals the inherent generality of this system for tracking and predicting age life effects. The time-temperature shift factor,  $a_T$ , is related to the activation energy of self-diffusion of atoms or molecules (Ferry 1971; Kaelble 1971.):

$$\Delta H_T = 2.303 R \frac{d(\log a_T)}{d(1/T)}, \quad (23)$$

where  $\Delta H_T$  = activation energy for self-diffusion,  $R$  = gas constant,  $a_T$  = time-temperature reduction factor, and  $T$  = absolute temperature (K). For the special case where the derivative,  $d(\log a_T)/d(1/T)$ , remains constant over a range of temperature, equation (23) becomes equivalent to the standard Arrhenius expression for activation energy. The self-diffusion kinetics in many physical systems obey more complicated laws. For example, the kinetics of segment

motion in amorphous rubbery polymers have been shown to be well described by an equation due to Williams, Landel, and Ferry (WLF) which has the following form (1955):

$$\log a_T = \frac{-17.4(T-T_{go})}{51.6+T-T_{go}}, \quad (24)$$

where  $T$  = temperature of measurement (K), where  $T > T_{go}$ , and  $T_{go}$  = characteristic glass transition temperature of the polymer. Differentiation of Eq. (24) provides the following relation:

$$\Delta H_T \left( \frac{\text{kcal}}{\text{mole}} \right) = 2.303 R \frac{d \log a_T}{d (1/T)} = \frac{4.12 T^2}{(51.6+T-T_{go})^2}. \quad (25)$$

Equation (25) is seen to predict a rapid variation in  $\Delta H_T$  at temperature slightly above  $T_g$ . At higher temperature where  $T-T_g \gg 125K$ , equation (25) predicts a nearly constant value of  $\Delta H_T$  with changing temperature which follows classical Arrhenius definitions.

Modern theories of atomic or molecular self-diffusion clearly delineate the physical significance of equation (24) or equation (25) in terms of free volume models and largely replace the older theories which predict a simple Arrhenius type activation energy for self-diffusion in polymeric systems (Ferry 1971; Kaelble 1971.). The time-temperature shift factor,  $a_T$ , is explicitly related to effects of temperature upon the rheological response of a system. Experiments designed to isolate  $a_T$  must by definition hold  $a_c$  and  $a_M$  constant. In other words, over the temperature-time range where the experimental study evaluates  $a_T$ , a chemically and mechanically invariant system is being described. Rheological studies that evaluate  $a_T$  and  $\Delta H_T$  are normally conducted under inert environments and at very small amplitudes of stress and strain (Ferry 1971). The information gained by non-destructive studies of rheological response of a system may then be reintroduced into the experimental analysis which treats added effects of mechanical or chemical damage.

The general effect of mechanical stress in accelerating a failure

process can be treated by an extension of the diffusion controlled kinetics that determine the temperature-time shift factor. The time shift factor,  $a_M$ , due to mechanical stress (or hydrostatic pressure) provides potentially important contributions to the overall kinetics of failure. One well recognized influence of hydrostatic pressure on polymeric systems is related to the increase in both crystalline melting temperature,  $T_m$ , and glass transition,  $T_g$ , with increased hydrostatic pressure as described by the following relations (Ferry 1971; Kaelble 1971.):

$$T_m = T_{mo} + \left( \frac{\partial T_m}{\partial P} \right)_T P \quad (26)$$

and

$$T_g = T_{go} + \left( \frac{\partial T_g}{\partial P} \right)_T P, \quad (27)$$

where  $T_m$  and  $T_{mo}$  = the respective crystalline melting temperatures at pressure  $P$  and  $P = 0$ ,  $T_g$  and  $T_{go}$  = the respective glass transition temperatures at pressure  $P$  and  $P = 0$ , and  $P$  = hydrostatic pressure. The total pressure on an isotropic body can be described by the following relations (Kaelble 1971):

$$\bar{P} = P - \bar{\sigma} \quad (28)$$

and

$$\bar{\sigma} = \frac{1}{3} (\sigma_1 + \sigma_2 + \sigma_3), \quad (29)$$

where  $\bar{P}$  = total pressure,  $P$  = hydrostatic pressure,  $\bar{\sigma}$  = mean hydrostatic stress, and  $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$  = orthogonal tensile stresses in the 1, 2, 3 axis of cartesian space. When  $\bar{P}$  of equation (28) replaces the conventional hydrostatic pressure  $P$  in equation (26) and equation (27), one obtains (Kaelble 1971):

$$T_m = T_{mo} + \left( \frac{\partial T_m}{\partial P} \right)_T P - \left( \frac{\partial T_m}{\partial \bar{\sigma}} \right)_T \bar{\sigma} \quad (30)$$

and

$$T_g = T_{go} + \left( \frac{\partial T_g}{\partial P} \right)_T P - \left( \frac{\partial T_g}{\partial \bar{\sigma}} \right)_T \bar{\sigma}. \quad (31)$$

The physical process by which hydrostatic pressure  $P$  and tensile stresses  $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$  influence the kinetics of aging can generally be traced to the influence of these variables upon  $T_m$  and  $T_g$  transitions of the polymeric material (Ferry 1971; Kaelble 1971.). The effect of changing  $T_g$  of an amorphous polymer due to  $P$  or  $\bar{\sigma}$  is seen to change  $T - T_g$  in equation (24) even though temperature  $T$  is constant. It is desirable to isolate the mechanical effect, due to  $\bar{P} = P - \bar{\sigma}$ , from the temperature effect ( $T - T_{g0}$ ) upon the aging response of the material. For amorphous polymers, which display WLF type response, the magnitude of the mechanical time shift factor is given by the following relation:

$$\log a_M = - \frac{17.4(T - T_g)}{51.6 + T - T_g} - \log a_T, \quad (32)$$

where  $\log a_T$  is defined for the reference glass temperature,  $T_{g0}$ , by equation (24) and  $T_g$  of equations (31) and (32) describes the effects of  $\bar{P} = P - \bar{\sigma}$ . The activation energy for mechanical effects is thus described by the following relation:

$$\Delta H_M \text{ (kcal/mole)} = 2.303 R \frac{d \log a_m}{d(1/T)} = \frac{4.12 T^2}{(51.6 + T - T_g)^2} - \Delta H_T, \quad (33)$$

where  $\Delta H_T$  is defined for  $T - T_{g0}$  by equation (25) and evaluated at  $P \cong 0$  and  $\sigma_1 = \sigma_2 = \sigma_3 \cong 0$ .

Chemical processes normally alter a system in accordance with the following relation (Juve 1964):

$$\frac{dx}{dt} = K(c-x)^n, \quad (34)$$

where  $x$  = quantity reacted at time  $t$ ,  $c$  = initial concentration of reacting material,  $n$  = the order of the reaction, and  $K$  = the reaction rate constant.

Integrating equation (34) for first order reactions ( $n = 1.0$ ) provides:

$$K = \frac{1}{t} \ln \left( \frac{c}{c-x} \right). \quad (35)$$

For any other reaction order, where  $n \neq 1.0$ , integration of equation (34) provides

the following general expression:

$$K = \frac{1}{t} \left[ \frac{(c-x)^{1-n} - c^{1-n}}{n-1} \right] \quad (36)$$

Solving Eq. (36) for  $n = 2$  gives the relation:

$$K = \frac{1}{ct} \left( \frac{x}{c-x} \right) \quad (37)$$

A first order reaction provides a linear plot of  $n(c-x)$  versus  $t$  with a slope of  $1/K$ . A second order reaction produces a linear plot of  $1/(c-x)$  versus  $t$  with a slope  $K$ . Equation (36) provides a useful general expression for evaluating reactions with non-integer values for reaction order.

In aging studies a change in physical property  $M$  is often related to the extent of chemical change in the system by the following relations:

$$c-x = M_{\infty} - M_t, \quad (38)$$

$$c = M_{\infty} - M_0, \quad (39)$$

and

$$x = M_t - M_0, \quad (40)$$

where  $M_{\infty}$  = maximum (or minimum) value of physical property when reactants are exhausted,  $M_t$  = physical property at time  $t$ , and  $M_0$  = physical property at time  $t = 0$ . Very often, a readily measured mechanical property such as modulus or hardness is described by physical property  $M$  of equations (38) through (40). Before exploiting the use of mechanical measurements to follow chemical kinetics, it is mandatory to conduct a rheological experiment under inert conditions, where  $x = 0$  and  $\bar{I} = 0$ , to establish the time-temperature dependence of physical property  $M_t$ . Omission of this rheological characterization of  $M_t$  often diminishes the precision of the subsequent chemical kinetics study.

The activation energy for chemical reactions normally follows Arrhenius definitions and can be described by the following relation:

$$\Delta H_c = 2.303 R \frac{d \log a_c}{d(1/T)} = \frac{4.576 T_1 T_2}{T_2 - T_1} \log (K_2/K_1), \quad (41)$$



where  $\Delta H_c$  = activation energy for chemical reaction,  $a_c$  = time-temperature shift factor for chemical reaction,  $R$  = gas constant,  $T$  = absolute temperature (K), and  $K_1$  and  $K_2$  = chemical reaction rates at respective temperatures  $T_1$  and  $T_2$ . Equation (41) implies that  $d \log a_c / d(1/T) = \text{constant}$ , and this result is generally obtained when the chemical reaction kinetics are properly isolated from the time-temperature shift factors  $a_T$  and  $a_M$  described by equation (18).

Mechanical service life may in special cases relate to time-dependent development of structure rather than loss of continuity. The Avrami rate equation for crystallization provides an excellent example of this case and has the following form (Avrami 1939, 1940; Miller 1965.):

$$F(C) = \frac{V_\infty - V_t}{V_\infty - V_0} = \exp(-Kt^b), \quad (42)$$

where  $F(C)$  = cumulative extent of crystallization at time  $t$ ,  $V_\infty$  = specific volume at infinite time  $t=\infty$ ,  $V_t$  = specific volume at time  $t$ ,  $V_0$  = specific volume at  $t=0$ ,  $K$  = rate constant, and  $b$  = exponent that relates with the dimensionality of the crystal growth process ( $b=1, 2, 3$ , respectively, for 1, 2, and 3 dimensional crystal growth). The comparison in form of equation (42) for structure formation due to crystallization and equation (18) for flaw growth is striking. The spontaneous and time-dependent process of crystallization may operate adversely on performance properties by producing embrittlement and consequent loss of strength and toughness. It is evident the general design of experiments to study embrittlement due to crystallization closely correlated with experiments for flaw growths.

The process for isolating  $a_T$ ,  $a_M$ , and  $a_c$  in equation (18) depends upon fundamental physical and chemical criteria and is independent of the property selected for measurement. Therefore, the basic format for design of the accelerated aging conditions -- with regard to temperature, mechanical, and chemical exposure -- depends more upon the material composition than upon the property measured.

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## CHAPTER 10

### TECHNOLOGY TRANSFER AND UTILIZATION

#### 10.1 Purpose

In this report the past, present, and future technology of structural adhesives for aerospace applications has been under review. Since a great volume of information exists about this field and it is diverse in its disciplines, it was deemed appropriate that a discussion of technology transfer and utilization be included. The purpose of this chapter is to assess the nature of the technology and suggest the most effective means for reporting and channeling it for utilization by appropriate government agencies and civilian industries. When known and used, these technological advancements will lead to general public benefit as well as thrust the field of structural adhesives into promising new directions. Clearly, technology is of no value until it is utilized. Therefore, the benefit or impact that the information contained in this report will have on the nation's aerospace adhesives technology will be in direct proportion to the effectiveness and timeliness with which this information can be transferred and properly utilized by the appropriate engineers and scientists.

In this chapter, a review of existing methods of technology transfer in the field of structural adhesives will be presented as will a list of problem areas. Finally, recommendations regarding technology transfer techniques, including some so-called "spin-off" benefits of this technology, will be listed.

#### 10.2 Technology Transfer

##### 10.2.1 General Status

It has been stated by Leshner and Howick (1966) that: "Traditional means of transferring technology--such as the intersectoral movement of knowledgeable people, corporate diversification, conventional library system, the college classroom, and the technical journal--while extremely important, are no longer wholly adequate." This situation is due primarily to the rapidly

increasing pace of new discoveries and the sheer volume of published literature that accompanies their discoveries. While this statement about technology transfer was made several years ago, it still holds true today.

On June 13-15, 1972, a National Symposium on Technology Transfer was held in Washington, D.C. The symposium included discussions of technological transfer and reviews of information resources. This was followed by workshops on technical subjects such as non-destructive testing, advanced manufacturing processes, advanced materials and composites, and discussions on design techniques and reliability procedures. The keynote of the symposium was sounded by Dr. Edward David, Jr., then Science Advisor to the President and Director of the Office of Science and Technology. In his address, the directive to all government agencies to conduct technology transfer programs was clear. It also was emphasized that the process of technology transfer must start at the worker level and be encouraged and carried through by the technical administrators of the programs.

The government and its agencies realized years ago the importance of technology and its effective utilization and have adopted continuing programs in the field of technology transfer. Among the more active programs are the following, few of which include structural adhesives information:

- NASA Office of Technology Utilization
  - a. Scientific and Technical Information Division (STID) -- collects and stores bibliographic information relating to aerospace activities
  - b. NASA Selective Dissemination of Information Program (SDI) -- a computer-based system for notifying individual scientists and engineers of new reports and journal articles of value in their particular work
  - c. Published Information
    - (1) Technology Utilization Notes
    - (2) Technology Surveys

- (3) **Special Publications: handbooks, conference proceedings, selected bibliographies**
- d. **NASA Regional Dissemination Centers (RDC) -- offer services such as:**
  - (1) **Application Engineering**
  - (2) **Retrospective Searching**
  - (3) **Selective Dissemination of Information for Distribution to Selected Organizations**
- e. **Conferences and Seminars**
- **Atomic Energy Commission**
  - a. **Division of Technical Information (DTI) Services -- publishes journals, abstracts, books**
  - b. **General Services -- publication of topical reports, technical journals and meeting papers; conduct special seminars and information meetings; provision of consulting services**
- **National Technical Information Service, Department of Commerce -- primarily a document sales agency; provides other information disseminating functions and services including:**
  - a. **Sale of reports based on government R&D; as mentioned in "Fast Announcements" and "Government Research Announcements"**
  - b. **Literature Searching Services**
  - c. **Selective Bibliographies**
- **Scientific Information Exchange (SIE) Smithsonian Institution (funded principally by the National Science Foundation):**
  - a. **Serves to catalog and distribute information about federal R&D proposal plans to all federal agencies to avoid duplication of effort and establish priorities**
  - b. **Provides detailed information about research (tasks) being conducted and sponsored by the various government agencies**



- c. Offers other services, such as preparation of R&D product catalogs and indexes, name searches of people working in a particular field.
- U. S. Department of Agriculture -- the county extension agent concept is an effective way of disseminating and exchanging information about agriculture-related technology.
- Pennsylvania Technical Assistance Program (PENNTAP), State of Pennsylvania -- a program to develop institutions within the state to disseminate technical information and assist local industry in obtaining and using state and federally generated technology. (Fox and Marlow 1971). The PENNTAP program is a Commonwealth of Pennsylvania-organized agency designed to function as a statewide scientific and technical information network dedicated to technology transfer and utilization. PENNTAP's services extend to Pennsylvania business, industries, municipalities, health organizations, government agencies, civic groups and individual entrepreneurs who can apply scientific and technical information to solve existing problems. The leadership role, taken by this PENNTAP program in technology transfer and utilization on the statewide level, is considered to be providing guidance in setting up federal programs in this field. A review of the present status of technology transfer policies between the state and federal agencies has been published by a task force appointed by the Council of State Governments (1972). This status review of federal and state agencies and programs in the field of technology transfer and utilization illustrates the importance that is being placed on these topics. Moreover, programs of this type are being expanded to cover more topics.
- TECH-TRAN -- a center for technology transfer for St. Louis. (Anon. 1972) This agency collects and disseminates technical

information from business firms, individuals, government organizations and others from the St. Louis area. Contacts with technology transfer agencies from other parts of the nation and from many sources throughout the world are also within the scope of this city agency.

#### 10.2.2 Present Status and Trends in the Aerospace Adhesives Industry

As mentioned in Chapter 4, during the 1960s the U.S. enjoyed undisputed leadership in the field of aerospace structural adhesives formulation and technology, largely through federally funded R&D programs. Maintenance of this leadership requires continual technological advances. This continued leadership, however, is becoming particularly difficult to maintain because the past 20 years have seen a steady flow of technology exported, either through U.S. subsidiaries set up overseas or by licenses or other means. Furthermore, the Japanese and the West Europeans have been particularly successful in recent years in closing this gap via their own internal research efforts. Adding to this problem, for at least the past five years, the domestic aerospace adhesives industry has been in a depressed financial condition. The cutbacks in government R&D spending, and the cancellation of major programs such as for the SST have contributed to this decline, as have the reductions in procurement levels of new adhesives for military aircraft and other hardware. Commercial airframe manufacturers are shifting their purchase priorities to lower-cost standard adhesives, rather than continuing their past major emphasis on new faster-curing, higher-strength, and heat-resistant structural adhesives.

As a result, none of the aerospace adhesive firms that have survived are presently able to maintain anything approaching their previous level of R&D staff, facilities, or output. Several of these firms have been sold or merged. All have suffered major reductions in highly skilled development personnel. All are now putting their best efforts, and are assigning their best remaining personnel, to diversification efforts, trying to reduce their dependence on aircraft contracts, or other defense or space-related markets. Still other U.S.

firms, which now possess the strongest R&D capabilities in the adhesives area, have a flat policy against soliciting government-related adhesives business. The general openness of technology (informational) transfer policies by the federal government has in essence created this situation. Most government technical documents and unclassified technical reports on all government-sponsored R&D are made readily available to overseas competition. In many cases, this "exported" technical information is more effectively analyzed and disseminated by foreign countries than by the technical community within our own country (NMAB 1973). It is difficult for U.S. companies to become interested in any item of new technology unless it can have some degree of proprietary position in it. Such is an inherent fault with "free" technological information. It would help, therefore, if the results of some government-sponsored research and development programs were published on a restricted basis.

It is evident that policies and procedures for technology transfer and utilization of government-sponsored R&D should be designed to benefit U.S. technology. Such policies should be given very careful review and analysis.

### 10.3 Steps in the Transfer of Aerospace Adhesives Technology

One can outline the steps in the technology transfer process as consisting of five stages:

1. Information resource
2. Transfer to appropriate user
3. Evaluation of technology
4. Utilization of technology
5. Assessment of technology

These steps will now be analyzed with respect to the technical transfer of information on structural adhesives for aerospace applications.

#### 10.3.1 Information Resources

In the field of structural adhesives, one central source of information and analysis is under development. Under DOD sponsorship, the PLASTEC group at Picatinny Arsenal, Dover, New Jersey, is being expanded to serve as

a structural adhesives information center. This presently small group compiles, evaluates, and reviews information; answers inquiries from all sources; and publishes reports on literature consolidations. For example, a state-of-the-art report is presently being prepared on the adhesive bonding of plastic matrix/high modulus fiber composites. The PLASTEC program does not supply inputs from journal sources. Its major emphasis is on reports of federally funded R&D, as well as on abstracts and preprints of technical conferences.

Many technical journals contain articles about adhesion and adhesives, and one must rely on a resource like Chemical Abstracts to get the most complete coverage of the field. One cannot be sure, however, that the Chemical Abstracts survey is complete, especially in the mechanical engineering and design aspects of structural adhesive applications. For this kind of information the Engineering Index might be a more appropriate resource.

Several scientific and trade journals focus specifically on adhesion and adhesives and serve as good sources of information. Among these are:

- a. Journal of Adhesion (Gordon and Breach publication)
- b. Adhesives Age (Palmerton publication)
- c. Journal of the Adhesives and Sealant Council
- d. Adhesion ( Bertelsmann Fachzeitschriften, GmbH,  
Schluterstrasse 42.1 Berlin 15, W. Germany)
- e. Journal of the Adhesion Society of Japan (Nippon Secchaku Kyokai  
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- f. Resin News (Incorporating Adhesives and Resins), (A. S. Connor  
and Company, Ltd., Surrey, England)

#### 10.3.2 Transfer to the Appropriate User

The process by which technology is transferred from its point of origin to utilization is extremely complex. In any event, the climate through which the information is transferred must be responsive, innovative, and receptive. Several media exist for the transfer of technological information from

the source to the user. While a vast amount of literature exists on structural adhesives, this literature must be read and understood. This is an individual effort.

More effective ways of conveying technology are through societies, meetings, conferences, and short courses. No societies, however, function for the sole purpose of analyzing and transferring information about structural adhesives for aerospace applications.

Established short courses and conferences (as of 1973) include:

- a. American Chemical Society -- short course on "Adhesion and Adhesives" (Skiest and Miron)
- b. University of Utah -- "Polymer Conference on Adhesion" (Einhorn)
- c. University of Wisconsin Extension -- "Industrial Adhesive Applications" (Nicholls)
- d. Center for the Joining of Materials -- in the process of being established at Carnegie-Mellon University, Pittsburgh, Pennsylvania, by the National Science Foundation.
- e. Gordon Research Conference on the Science of Adhesion
- f. American Society of Metals -- technical course on "Fundamentals of Adhesive Bonding"
- g. Programmed Learning Course -- "Fundamentals of Adhesive Bonding," Penton Education Division, Cleveland, Ohio

Societies concerned with adhesive technology are:

- a. ASTM through D-14 Committee on Adhesives
- b. Adhesives and Sealant Council
- c. Adhesion Society of Japan

Meetings and proceedings that cover adhesives include:

- a. American Chemical Society Symposia
- b. Society of Aerospace Materials and Process Engineers (SAMPE)

c. Society of the Plastic Industry

d. Society of Plastic Engineers

### 10.3.3 Evaluation of the Technology

Before information on structural adhesives becomes adapted into a functioning entity, it must be studied, reviewed, examined, evaluated, tested, and compared in laboratory or prototype simulations. At this stage, the technology is developed into creating a socially useful product by the individuals, agencies, or companies that not only possess the information, facilities, and knowledge but can effectively understand, implement, and exploit it.

### 10.3.4 Utilization of the Technology

The informational concepts and ideas transmitted and evaluated are reduced to practice. Benefits of the utilization of the transferred information are clearly expressed and can be observed as an exploitation of the technology. Now other companies, government, or the public in general can take advantage of the reduced-to-practice information. When this has occurred, one can say the specific field of technology that has absorbed and implemented the information has achieved a higher level of development.

### 10.3.5 Assessment of the Technology

Long-term assessment of technology is an important part of technology transfer and utilization. One must continually (1) review the overall benefits of technological advances to a specific field or industry, and (2) determine what effect this technological advance has on other technological fields and industries. An important phase of technology assessment is technology monitoring which involves watching young technology carefully to see how it is developing and adjusting to it as it changes. In this case social benefits (or detriments) often must be reevaluated.

### 10.3.6 Systems Approach to Technology Transfer

In this brief review of the steps involved in the process of information transfer and utilization, it is important to note that when new technologies are

discovered in the laboratory, pilot plant, or in the field, all five steps in the transfer process must be considered. In effect, one must employ a systems approach (Shane 1973). At the onset of information exchange, the overall impact that the technology will have on society is an important consideration. Technological forecasting must therefore also enter the picture.

#### 10.4 Problems Related to Technology Transfer and Utilization

In order for technology to be effectively transferred and applied, the specific social environment into which the technology is to impact must be receptive and preferably active. The potential users of new technology must be receptive to innovation and change. In addition, there must exist recognizable specific needs to which the technology can be applied.

In general there are inherent barriers to technology transfer that are neither financial nor technical. These barriers are: (1) unwillingness of management to take risks, and (2) inability of the technical community to communicate among themselves (inter-disciplinary language barrier) and with management.

##### 10.4.1 Problems Within DOD Agencies and Their Aerospace Contractors

- a. Existence of entrenched government specifications that are difficult to supplant with improved or updated technology
- b. Problems related to product liability
- c. Difficulty in evaluating advantages (or disadvantages) of new technology due to high cost
- d. Deterrent effects of proprietary design ownership
- e. Inter-agency rivalry
- f. Impact of security regulations
- g. Inability to communicate and present information in the proper form under established regulations and procedures

##### 10.4.2 Problems Related to the Transfer of Information to Private Industry

- a. Non-exclusive nature of federally funded R&D technology, except in some NASA and AEC programs

- b. Cost of evaluating new technology may be high
- c. Product liability factors

#### 10.4.3 Committee Survey on the Transfer and Utilization of Aerospace

##### Adhesives Technology

In an attempt to identify the most pertinent types of aerospace adhesives technology that should be transferred now and in the future, a survey of the members and liaison members of this report committee was conducted. In addition, the problem areas encountered in transferring this technology are also noted. The results of this survey are presented below. As indicated, it is proposed that two types of technology exist and must be dealt with in the area of structural adhesives: (1) presently known technology, and (2) proposed technology.

#### 10.4.3.1 Results of Questionnaire Survey of the ad hoc Committee

##### a. Adhesives Technology That Now Exists and is Not Being Utilized by the Aerospace Industry

- Elements and practice of fracture mechanics approaches to reliability and endurance of adhesive joints.  
Barriers: Interdisciplinary nature of adhesive joint concepts, inadequate educational training in the field, semantics barriers between adhesive technologists and adhesive bond designers.
- Test procedures exist to determine mechanical design parameters of adhesive joints.  
Barriers: Equipment needed is expensive and instrumentation (e.g., extensometer design) must be developed.
- Nature of metal surface oxides and how they influence the environmental durability of joints is understood.  
Barriers: Semantics barrier and lack of knowledge about surface chemistry with regard to aerospace manufacturing technologists.
- High and low temperature adhesives exist but are not being



utilized.

**Barrier:** Not enough use data and information exists and the present systems are not trusted.

- Curing technology exists in private industry to help solve some problems in aerospace adhesives technology.

**Barrier:** There is a fear that the government will require these private firms to release proprietary information about their adhesives if they get involved in government-sponsored programs.

b. **Suggestions for Overcoming Barriers to Transferring This Existing Technology**

- A structural adhesives design handbook should be written.
- The government should sponsor programs on the development of instrumentation to measure the design parameters needed in the engineering design of adhesive joints.
- Engineering education curricula should be changed to include courses on structural adhesive bonding.
- Instructional short courses should be established to serve to update aerospace engineers on the latest information on adhesives technology for aerospace applications.
- The format of government R&D reports should be changed to effect a more accurate evaluative interpretation of the work. Perhaps the work could be reviewed by an impartial panel.
- Changes should be made in the government's attitude toward proprietary information when dealing with private industry.
- A system should be set up to provide for more effective abstracting and circulation of information about aerospace

adhesives. The publication and distribution of information about new successful uses of structural adhesives in the aerospace industry should be publicized.

c. Adhesives Technology That Will be Developed in the Future

- A vast amount of adhesive joint design information will become available.
- Reliable and durable adhesives will be developed and their service life will be known. This will give structural design engineers more confidence in using adhesives.
- Better test procedures and test equipment will be available; the adhesive joints and adhesives themselves will be much better characterized.
- New adhesive polymers and curing agents will be developed leading to reliable cold bonding adhesives.

d. Impact of This New Adhesives Technology on the Aerospace Structural Adhesives Industry

- More adhesives will be used for primary structure applications.
- Bond in place (durable cold bonding) adhesives will be developed and will solve the problem of field repair and retrofit service of aircraft.
- This future work will lead to a greater confidence in the use of adhesives and will thus increase the use of adhesives in aerospace applications.

e. Benefits of the Future Aerospace Adhesives Technology to Other Industries - Technology "Spin-Offs"

The development of this proposed new adhesive technology will aid in a wide number of industries -- namely, automotive and

trucking, building and construction, marine and shipboard applications. The proposed work would assist the entire field of the joining of materials.

f. Barriers to the Transfer of This Future Technology and Ways of Overcoming These Barriers

The barriers that would be encountered in transferring this future technology are the same as those for known technology. One would expect, however, that if the proposed educational strategy is carried out, the transfer of this future information will not be beset by semantics and interdisciplinary barriers.

The ways of overcoming these barriers also follow the same means as for known technology. The Committee again clearly emphasizes the need for a comprehensive adhesives handbook and design guide.

10.5 Conclusions and Recommendations

10.5.1 Purpose

Conclusion: There exists no centralized, complete information resource that consolidates literature, technical information, and data on aerospace structural adhesives and bonded joints.

Recommendation: The PLASTEC group at Picatinny Arsenal, Dover, New Jersey, should be assigned to function as a comprehensive technical information and analysis center on structural adhesives. Primary access to this information service should be limited to domestic industries and be on a minimum - or no-cost basis (not required to be self-supporting). This information center should benefit not only the aerospace industry but all other U.S. manufacturers and users of structural adhesives.

10.5.2 Technology Transfer

Conclusion: The present methods of transferring or conveying structural adhesives information and technology to the proper aerospace

industrial community are not adequate because of the fragmentation and interdisciplinary nature of the field.

**Recommendation:**

- a. A structural adhesives bonding handbook that will serve to consolidate the most recent established information on structural adhesives and joints should be prepared, reviewed, published, distributed, and maintained up to date. This will lead to a better understanding of adhesive joint design and help the industry to incorporate the most current design information into their aerospace structures.
- b. The NSF-supported Institute for the Joining of Materials (Carnegie-Mellon University) should be encouraged to carry out basic research programs on collection and distribution of all technical information on structural adhesives materials and engineering technology. Its capabilities and resources should be assessed with regard to its ability to undertake the task of compiling the proposed design handbook on structural adhesives. Through cooperative programs, this Institute can serve as one of the major academic centers for structural adhesives research. The coordination of educational programs (short courses, technology transfer seminars and workshops) should evolve from this activity.
- c. The appropriate federal government agencies should sponsor more interagency programs, seminars, workshops, and meetings specifically on aerospace adhesives, with the participation of industry. This will enable DOD agencies and industries to obtain a better overall view of the needs and trends in aerospace adhesives technology, and serve as a platform that will increase the probability of possible "spin-off" utilization of the technology.
- d. An ad hoc committee should be established to monitor and suggest improvements in the rate of the technology transfer and

utilization process in the structural adhesives field.

**10.5.3    Steps in the Transfer of Aerospace Adhesives Technology**

**Conclusion:** Adapting new information on structural adhesives into a useful technology is often a time-consuming and expensive process.

**Recommendation:** In appropriate circumstances, financial and technological assistance should be given by the federal government to assist industry in exploiting new ideas and evaluating present technology on aerospace adhesives and their applications. Possible means for accomplishing this recommendation should be examined, since this arrangement will benefit the government by increasing the willingness of all industrial concerns to carry out government R&D programs on structural adhesive applications.

**10.5.4    Problems Related to Technology Transfer and Utilization**

**Conclusion:** The transfer of government-developed aerospace adhesives science and technology within DOD agencies and their contractors proceeds at too slow a pace.

**Recommendation:**

- a. Establish a continuing series of government-certified short courses in the field of aerospace adhesives technology. Let this course serve to update in an interdisciplinary way the technical community in the field of structural adhesives.
- b. Government purchase orders for aerospace equipment and materials should specify the requirement that appropriate personnel in the bidding firm be certified aerospace adhesives technologists who have completed the (updating) course as described in recommendation a.
- c. Direct an appropriate competent agency to perform a critical review of government regulations regarding military specifications in the structural adhesives field and propose ways in which new materials and technologically-advanced concepts can more systematically replace outdated technology.

- d. To facilitate technology transfer on structural adhesives, a "personal champion" should be sought for new items of technology as they arise.

#### 10.5.5 Conclusions and Recommendations

Conclusion: Developed, reduced-to-practice aerospace adhesives technology and information is not being effectively utilized by other civilian industries. The automotive, building and construction, and marine industries are some potential "spin-off" users of this structural adhesives technology.

Recommendation: A Delphi analysis relative to determining the overall utility of the existing aerospace adhesives technology in other applications should be conducted. The results of this analysis should be conveyed to the appropriate trade associations for distribution.

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